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MELLOR'S MODERN  
INORGANIC CHEMISTRY

A ~~COMPREHENSIVE~~ TREATISE ON  
INORGANIC AND THEORETICAL  
CHEMISTRY

By J. W. MELLOR, D.Sc., F.R.S.

16 Vols. with supplements

Vol. I.	H, O.
Vol. II.	F, Cl, Br, I, Li, Na, K, Rb, Cs.
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Vol. II, Supplement I. F, Cl, Br, I, At (The Halogens)

*In preparation*

Vol. II, Supplement II The Alkali Metals

# MELLOR'S MODERN INORGANIC CHEMISTRY

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*With diagrams and illustrations*

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## PREFACE TO THE 1961 EDITION

MELLOR'S *Modern Inorganic Chemistry* has undergone many revisions since its first appearance, and in 1939 very extensive changes and rearrangement of its contents were made and it was largely rewritten by the present editor in collaboration with Dr. Mellor himself. Nearly ten years have now elapsed since the last completely new edition was issued and the developments of the intervening years have more than justified a further thorough overhaul of the work.

There is some division of opinion at the present time as to whether current ideas about the nature of matter and the structure of the atom should be assumed and taken as the basis from which the rest of chemistry should be developed or whether the evidence for these accepted views should first be discussed and the logical conclusions developed from it. In this present edition an attempt has been made to meet both points of view by including a new chapter, immediately after the introductory historical one, summarizing present ideas, before embarking upon the succession of chapters, as in the earlier editions, setting forth chronologically the accumulation of the evidence.

Another change in this edition has been the division of the chapter on "The Constitution of Matter" into two; one covers this topic proper and the other "The Outer Sphere of the Atom" dealing with valency and chemical behaviour. This is now followed by a chapter on "Nuclear Chemistry" which covers transmutation, nuclear fission, nuclear fusion, atomic piles and other applications of atomic energy. This has enabled the old chapter at the end of the book on "The Radio-Elements" to be eliminated and its subject-matter to be treated in a more logical order, as the chemistry of the radio-elements can now be dealt with along with that of the corresponding related stable elements.

The book as a whole has been carefully scrutinized and revised where necessary, in order to bring it up to date.

I acknowledge with gratitude valuable assistance from many quarters including Imperial Chemical Industries, Ltd. (notably the General Chemicals, Salt, and Alkali Divisions), Laporte Chemicals, Ltd., Magnesium Elektron, Ltd., the Steetley Magnesite Co., Ltd., the Washington Chemical Co., Ltd., The Woodall-Duckham Construction Co., Ltd., and the Southern Gas Board, all of whom have been unsparing in their efforts to provide information and diagrams; the sources of these latter are indicated, in each instance, in the text.

I am also deeply indebted personally to many colleagues and friends for valuable criticisms and suggestions and to numerous correspondents who have taken the trouble to point out errors which had otherwise escaped detection. I am especially indebted to Mr. J. M. Harrison for constant and unstinted expert advice and encouragement, to my former

pupil, Mr. N. J. Maggs, who has read through the whole of the proofs, and to my secretary, Miss Margaret Elliott, for invaluable assistance in many ways and especially in the preparation of the Index.

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*March 1961*

## EXTRACT FROM PREFACE (1939 Edition)

THIS new edition of Mellor's *Modern Inorganic Chemistry* embodies extensive changes in comparison with the previous editions; changes which have been indicated in part by criticisms of the older issues, and in part by the extensive development of the subject since the book was first written.

Mellor's *Modern Inorganic Chemistry* was first published in 1912 and very quickly achieved widespread popularity in many parts of the world. It had run to eight editions, several of which had been issued in more than one impression, when it became clear that in preparing a further edition the time had come for a drastic revision and rearrangement of its contents. The present volume is the consequence. By the time that this decision had been made, Dr. Mellor was, unfortunately, in failing health, and this in conjunction with his very numerous commitments made it necessary for the work of revision to be undertaken jointly. Although Dr. Mellor passed away before it could be published, he had given a final revision to the whole of the joint work in manuscript form; so that the new edition is now issued with the confidence that it has his full authority.

The most obvious change which has been made is in the arrangement of the contents; this is now so markedly different from that adopted in the older editions that the book has had to be almost entirely rewritten. The plan now adopted begins with a series of chapters (1 to 16) covering all the necessary general and theoretical parts of the subject, starting from the properties of gases and proceeding by logical steps to the Atomic Theory, modern views of the Structure of Matter, the Electrolytic Dissociation Theory, and so forth. There then follows a group of seven chapters (17 to 23) devoted to the elements hydrogen, oxygen, carbon, nitrogen, sulphur and the halogens, and their principal compounds. These elements, for the most part, do not fit very satisfactorily into a treatment strictly according to the Periodic Table, but they do comprise a large portion of the chemistry of any more or less elementary course. The remainder of the elements, and their compounds, are then discussed according to the order of the groups of the Periodic Table.

Another change in arrangement concerns the descriptions of salts. These are now given under the heading of the metal concerned; their treatment under the acids in the earlier editions had given rise to considerable criticism. A standard order has also been adopted for the salts of each metal, so that rapid reference may be facilitated.

The principal further difference concerns the diagrams. A large proportion of these is new, and those which are not new have been redrawn. A number of new half-tone illustrations has also been included.

In carrying out the rewriting and revision I have attempted to preserve a proper balance between theories and the facts on which they are based. Dr. Mellor and I were both of the opinion that there is a tendency at present to give the former undue prominence and to treat the facts as of lesser importance. Experience as examiners has shown us that candidates for scholarships and the like are frequently well versed in the latest theoretical developments and yet have, at best, only a vague knowledge of the chemical behaviour, or the preparation, of common substances. I hope that the treatment now set forth will prove satisfactory in this respect.

Thanks are due to various authors and examining bodies for permission to use quotations, and questions from examination papers. The source of each of these is indicated where they occur in the text. My own personal acknowledgments are due to many friends and colleagues for valuable help and advice and in particular to Mr. J. M. Harrison, M.A., Dr. H. Irving and Mr. A. Weston, M.Sc. I have to thank Mr. Weston also for reading through the whole of the proofs. My thanks are further due to Mr. N. Wilson for assistance with the preparation of the index.

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Oxford  
*March 1939*

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## CHAPTER 1

### INTRODUCTION

Let us remember, please, that the search for the constitution of the world is one of the greatest and noblest problems presented by nature.—G. GALILEI.

Il est regrettable que les traitées modernes négligent l'histoire et présentent comme des monuments achevés des science en perpétuelle évolution.—F. OSMOND (1906).

#### § 1 Chemistry as a Branch of Science—The Aim and Meaning of Science

THE answer to the question, "What is chemistry?" begins by saying that chemistry is a branch of natural science—or science, as it is more often called. What then is science, and what is its meaning?

Science embraces the sum total of human knowledge, and it ranges over the whole realm of nature. Science is not merely a mass of empirical knowledge gained by observation and experiment, but it is an organized body of facts which have been co-ordinated and generalized into a system. Science tacitly assumes that nature is a harmonious unity, and that rational order pervades the universe. Science seeks a complete knowledge of the multitude of interrelated parts of the universe which act and react on one another producing endless variety.

The edifice of science thus rests upon a foundation of reliable facts. Each of us in his or her daily life receives, through the senses of sight, touch, hearing, etc., many sensations, and through these sensations is made aware of many facts. These facts when stored in the memory constitute our individual stock of knowledge. Recorded, and their reliability ascertained, they comprise the accumulated knowledge of our civilization—but *they* are not science. This knowledge is sometimes known as empirical knowledge; it describes facts. Science begins by comparing facts. Empirical facts, in consequence, can form a science only when they have been arranged, rearranged, grouped, or classified so as to emphasize the elements of similarity and identity in different phenomena. Accordingly Thomas Hobbes expressed the opinion that the main purpose of science is the tying of facts into bundles. This bundle-tying, indeed, forms no small or insignificant part in the development of science; otherwise expressed, a significant advance has been made in the development of a science when the observed facts have been codified into a system so that a medley of empirical facts is systematically summarized under a small number of heads. The process of classification and correlation is one of the methods of scientific investigation. Knowledge so systematized is scientific knowledge.

## § 2 Experiment

In order that knowledge may be correlated, arranged and classified into a science, it is essential that the reliability of the facts concerned should be ascertained. Much of the so-called science of ancient times and of the Middle Ages is rendered worthless by neglect of this essential precaution. It is very likely true that few people in these periods really *believed* the more fanciful of the stories then current, but mere disbelief in itself is of little avail—truth is often stranger than fiction. What was lacking was the desire or inclination to *test* the truth of these statements. Stories were repeated by writer after writer without even the slightest attempt at verification.

In the modern period, such statements are submitted to the test of *experiment*. Experiment is the handmaid of science for it is really a method of *observation* which is employed either to test the validity of a recorded statement or when the facts are so masked by other conditions that they cannot be accurately observed unless the obscuring conditions are suppressed. The chemist would not make much progress if it were only possible to observe phenomena just as they occur in nature, and not possible to make observations under controlled conditions. By experiment, it is possible to make combinations of different forces, and different forms of matter which are not known to occur in nature; to eliminate complex disturbing conditions; and to observe phenomena under simplified conditions. An experiment has been well defined as *une observation provoquée*. Experiment is useful only when there are conditions which obscure direct observations. The most successful experiment does no more than make a fact which was previously obscure as patent as one that was open to direct observations from the first.

## § 3 Scientific Method—Hypotheses, Theories, Laws

As has been said, facts (whether collected by direct observation of nature or as the result of experiment) are not science, only knowledge. The method of science is to work upon these facts and upon them to found hypotheses; that is, to put forward suggestions for (or guesses at) explanations or general principles which will serve to connect and correlate a certain body of facts.

It is a popular belief that the aim of science is to explain things; as a matter of fact, the so-called explanations of science do not usually get much beyond describing the observed facts in the simplest possible terms so as to make their relations with one another clear and intelligible. The description may emphasize the history of a phenomenon, or the conditions under which the phenomenon occurs: in other words, science may explain a phenomenon by describing how one event is determined by an antecedent action—sometimes called a **cause**; and how one particular set of conditions—the cause—can

give rise to another set of conditions—the **effect**. Science explains a phenomenon (the effect) by showing that it is a necessary or rather a probable consequence of another phenomenon (the cause).

Although every effect may be traced to a previous event as its cause, in the physical world phenomena follow one another as links in an unbroken chain of cause and effect. It is soon recognized that the cause of a phenomenon is an effect which itself needs explaining by some ulterior cause, so that causes can be traced backwards in a never-ending chain of events. Owing to the limited range of man's understanding in a world of infinite complexity, we are far, very far, from comprehending the true conditions, the true causes, or the true reasons for natural phenomena.

The mind cannot receive a long series of details without encircling and connecting them by a common bond which is a kind of *mental nexus*; similarly, in the attempt to find the causes of many phenomena, man is compelled to build an imaginary model showing how a given set of conditions—the hypothesis or theory—is always followed by particular effects. A phenomenon is then explained by showing that it is bound to occur by the operation of the set of conditions postulated by the hypothesis. Consequently, hypotheses are essentially guesses at truth. The rational observer does not trust to random guesses, but he is guided by a more or less vague intuitive conjecture (hypothesis) as to the meaning of the phenomena under investigation, and experiments are devised accordingly, for

Man's work must ever end in failure,  
Unless it bear the stamp of mind.  
The head must plan with care and thought,  
Before the hand can execute.—SCHILLER.

The next step is to test the hypothesis by using it to predict what ought to take place in a given set of conditions if it be true. These predictions are then submitted to the test of experiment. An hypothesis thus serves to prompt new experiments and to indicate the conditions under which the search for new facts is likely to be successful.

If, on the one hand, this testing by experiment fails to confirm its predictions, the hypothesis must be discarded and a new one framed and similarly tested. On the other hand, if experiment shows its predictions to be correct, it ultimately becomes a theory and thus an important part of science, for some of the facts which constitute knowledge have thus been co-ordinated and generalized into a system.

A theory must, however, still be submitted to the test of prediction and verification by experiment, and if, and when, new facts come to light which are inconsistent with the theory, it must, like an unsatisfactory hypothesis, be discarded or severely modified. But if every fresh testing serves to confirm the theory and to put its truth virtually beyond doubt it is then called a Law.

The process, therefore, of elevating an accumulation of facts into a science consists in the framing and testing of hypotheses, theories

and laws. An hypothesis is a guess which, if true, will explain a given set of phenomena; a theory is an hypothesis the truth of which, after testing, is apparently established; and a law is a theory which has stood the test of new facts and of experiment so successfully that its truth is established beyond any reasonable doubt.

To sum up, *science* is *knowledge* organized, correlated and generalized into a system. The *method* of science consists of the four stages:

- (i) observation and experiment for the discovery of facts;
- (ii) classification and comparison of these facts;
- (iii) the framing of hypotheses to account for the facts;
- (iv) the testing and verification of hypotheses, resulting ultimately in the making of theories and laws.

#### § 4 Branches of Science

Science, framed from the facts of nature as already described, is a coherent unity; but the sum total of human knowledge has now grown too vast to be comprehended in its entirety (even when classified and co-ordinated into a system) by any one man's mind. The limitations of the human mind thus make it necessary to divide science artificially into departments, or branches, for the purposes of study and investigation. These divisions are, of course, arbitrary; for "the divisions of the sciences," as Francis Bacon has said, "are like the branches of a tree that join in one trunk." Chemistry is such a branch of science—others are astronomy, physics, geology, biology and so forth.

The science of chemistry is concerned with the composition and properties of the different kinds of matter in the Universe; with the ultimate constitution of matter and of the phenomena which occur when the different kinds of matter react with one another.

#### § 5 The Early History of Chemistry

Chemistry as a *science* in the sense we have been using that word is of comparatively modern growth, for no systematic study of the phenomena comprised within our definition of chemistry can be said to have been made until the seventeenth century. But many of the familiar operations of experimental chemistry were practised in ancient times—in fact, chemistry as an *art* is very old.

It is impossible to say when the craft of chemistry originated; its beginnings are lost in the mists of antiquity. The extraction of the common metals from their ores—a crude kind of chemistry—is known to have been carried out for a very long period of time, and the preparation of active principles derived from plants for use as drugs, involving the use of many processes now associated with the practice of chemistry, has long been an important feature, even of primitive civilizations.

The great Greek philosophers were in no sense practical men; they

had no interest in the collection of facts by experiment nor in the practical verification of the results of their philosophical speculations; but at the same time it is in their writings that we find the first indications of anything approximating to a *science* of chemistry.

Thus Democritus (*ca.* 400 B.C.) suggested an atomic theory of the constitution of matter: it is true that it was vague and based on very little in the way of reliable fact; but nevertheless it was an attempt to co-ordinate and explain what were believed to be facts about the behaviour of matter, and, in that very limited sense, it was a contribution to the beginnings of the *science* of chemistry.

The same is true of Aristotle's four-element theory: another attempt (based on a meagre foundation of fact and a large amount of philosophical theorizing) to explain the nature of matter. According to this theory, which was more or less current for 2,000 years, all matter consisted of a kind of primordial substance (which was really matter as we know it shorn of its "properties") to which had been added varying amounts of the four "elements," earth, air, fire and water. The word element was clearly used in a sense different from that in which it is now employed in chemistry; the modern conception of an element is really due to Robert Boyle (*see* page 54). To the follower of Aristotle, the term element implied a *quality* rather than a *kind* of matter. It is in this sense, perhaps, akin to the use of the word in the phrase "there is an *element* of truth in a given assertion." Thus, the element earth represented the qualities of coldness and dryness; air, those of hotness and wetness; fire, hotness and dryness; and water, coldness and wetness. The long survival of theories of this type was due largely to the lack of any desire to test them; but partly also to their very vagueness which, in the absence of the means for real quantitative work, would have rendered disproof difficult, even if it had been attempted.

That many essentially chemical operations and methods were known and practised in classical times is clear from many of the writings of the period which have come down to us. Thus, Pliny's famous treatise on "Natural History" contains, *inter alia*, many *facts* of chemistry, and also describes a great many chemical processes, such as the extraction of metals from their ores and the preparation in a state of purity of many common substances such as alum, white lead, and so forth. Many similar records are to be found in the writings of the classical period; but they are collections of recipes for the making of useful substances and descriptions of technical arts and crafts of the time and in no sense do they contribute anything to the *science* of chemistry.

Similar accounts are found in the works of a number of writers of Alexandria and the northern portions of Egypt during the first few centuries of the Christian era, and here we find the first beginnings of the traditions of alchemy. It is here, too, that there occurs the first mention of the "Sacred and Divine Art" and the earliest use of the word "Chemeia" for it. The "School" of chemical craftsmen who

lived at this period in Alexandria and surrounding districts of Northern Egypt probably had its origin in a fusion of the philosophical speculation of Greece with the practical knowledge of the Egyptians. The latter had a great tradition in the working of metals and glass and in the dyeing of fabrics.

### § 6 The Alchemists

The Egyptian and Byzantine period may be considered to have comprised the first six or seven centuries of the Christian era. Some of the earlier writers such as Zosimus (*ca.* 250–300), Democritus (not the Democritus referred to on page 5 as having propounded an atomic theory, but another) and Mary the Jewess (who has been credited with the invention of the water-bath, still known as *bain-marie* in France) were evidently practical people with experience of the laboratory and its problems; but the later authors were either content to write about alchemy without practising it, or else were too obsessed with the idea of making gold to trouble about mentioning anything which did not appear to have a bearing on this problem.

Egypt was conquered by the Arabs in A.D. 640 and so the Greek writings on alchemy passed to Arabia and were soon translated into Syriac or Arabic, possibly both.

The Arabs were a practical race and a good many discoveries of chemical importance were no doubt made by them. Perhaps the most important of the Arabian alchemists was Abu Musa Jabir ibn Hayyan al Sufi, commonly called Geber (eighth century A.D.). What purport to be translations of his works into Latin appeared in the twelfth century; but there are conflicting views as to how far, if at all, these Latin translations are really based on Geber's writings. It seems likely, however, that at least a certain number of discoveries attributed to Geber in the Latin "translation" are there wrongfully attributed to him and were actually made at a much later date. Other notable alchemists of the time were Rhazes (*ca.* 900) and Avicenna (*ca.* 980).

The knowledge acquired by the Arabs from Graeco-Egyptian and Byzantine sources, and extended by themselves, gradually percolated into Europe, and in the twelfth and thirteenth centuries translations of Arabic works began to be made, especially in Spain, and the "profession" of alchemy soon rose to a position of considerable importance. Among the great names of the period may be mentioned Albertus Magnus (1193–1280), Roger Bacon (*ca.* 1214–1294), usually considered to have been the discoverer of gunpowder in the West, Raymond Lully (1235–1315?), discoverer of the method of making pure alcohol, and Arnold of Villanova (1234–1312).

This period saw the development of the idea of the three alchemical elements, mercury, sulphur and salt, into the current thought of the day. Geber (according to the Latin version) had taught that metals are composed of mercury and sulphur from which they are generated in the interior of the earth. Gold and silver were supposed to contain



a pure mercury and a "clean" sulphur; while other metals contained an "unclean" sulphur. It was thus supposed that base metals could be converted into gold and silver by altering the proportions of mercury and sulphur in them, and by "cleansing" the sulphur. This was the theory underlying the traditional pursuit of alchemy, the finding of the philosopher's stone which would transmute the baser metals into gold or silver.

According to the three-element theory of the later alchemists, sulphur was the principle of combustibility, salt the "fixed part" left after calcination, while mercury was the principle of metallicness contained in all metals. The conception of an element implicit in these theories is still largely that of the Greeks and far removed from the modern meaning of the term.

### § 7 The Iatro Chemists

About 1525 there arose a new school of quasi-chemists usually known as the "Iatro Chemists" or "Medical Chemists." Their aim was to discover the "Elixir of Life" which would cure all diseases and confer the boon of perpetual youth. It was thought by some that the Elixir of Life and the Philosopher's Stone would turn out to be the same; partly no doubt because of the idea that to change a base metal into gold involved a kind of healing.

The founder of Iatro-chemistry was Paracelsus (Philip Aureolus Theophrastus Bombast von Hohenheim) (1493-1541), whose chief distinction was that he demonstrated the value of many substances for use as medicines and so directed the minds of alchemists from the attempt to manufacture gold to other and more profitable ends.

The beliefs and writings of Paracelsus were, however, steeped in superstition, but among the successors were some, notably Libavius (1540-1616) and Van Helmont (1577-1644), who, though still credulous and superstitious, were yet men with something of the scientific spirit. Van Helmont is to be remembered particularly for the invention of the word "gas" and for being the discoverer of carbon dioxide.

Some important works written under the *nom de plume* Basil Valentine, probably in the sixteenth or seventeenth century, were for a long time wrongly supposed to have been the work of a fifteenth-century Benedictine monk before Paracelsus. Anachronisms in the supposed writings of Basil Valentine show that these could not have been written so early as the fifteenth century and the imposition of Basil Valentine as a pre-Paracelsian writer has been called a "seventeenth-century hoax."

### § 8 The Birth of Modern Science

The course of European history during the sixteenth and seventeenth centuries was to a considerable extent determined by the birth of a

new spirit of inquiry: that new attitude of mind and thought associated with that great movement which is called the "Renaissance." There arose at this time a spirit of inquiry which sought to understand the reasons for the beliefs men held, and a desire to seek after knowledge and the truth for its own sake. The intallibility of the past ceased to be a dogma, and the Renaissance, from which historians date the beginning of their modern period, was also the beginning of the period of modern knowledge and modern science.

Francis Bacon (1561-1626), who published in 1620 a work—*Novum Organum scientiarum*—in which he sought to define the true method for obtaining knowledge, is sometimes called the "Father of Modern Science." He explained what he believed to be a new way of attacking scientific problems. In his method, the first stage is the accumulation of facts, to be obtained by direct observation, and to be scrutinized critically in order to be free, so far as possible, both from errors of observation and from errors due to the predilections of the observer. The second stage is the survey of these facts and the search among them (without any attempt to make them fit in with a preconceived theory or philosophy) for those likenesses and differences from which the conceptions of the common properties and "laws" are to be formed. Bacon thus advocated the method of exclusion, or of deductive induction. This is Bacon's great contribution to science, and although his method of induction is only rarely consciously employed in scientific work, it nevertheless lies at the root of all scientific thinking; in addition he is to be remembered for his insistence on the importance of careful observation, of the collection of facts, and of the necessity for the utmost impartiality and open-mindedness in the correlation and co-ordination of observations.

If Bacon were the founder of modern science, Robert Boyle is usually thought of as the founder of the *science* of chemistry. He was probably the first to study it for its own sake and not for the sake of making gold or medicines (here we see the real spirit of the Renaissance in operation); he it was who introduced into chemistry a really rigorous experimental method for the testing of theories and for the ascertainment of the reliability of facts; and to him is due that conception of an element with which we are familiar. He demonstrated the falsity of the Aristotelian and Alchemical doctrines of elements by showing that by no method available could these so-called elements be extracted from substances supposed to contain them; and gave as a definition of an element "the practical limits of chemical analysis." That is to say, elements are substances incapable of further decomposition by any means available at a given time. He recognized that substances at one period regarded as elements might later, with the availability of new methods of attack, prove not to be so, but that until such a happening had occurred they must continue to be thought of as elements. Examples in modern times of the reality of this contingency can be quoted, as, for instance, the resolution by von

Welsbach in 1885 of didymium into neodymium and praseodymium (see page 757). Boyle thus laid the foundations on which Lavoisier and Dalton were to build a century afterwards.

The intervening period was occupied with the rise and development of the Phlogiston Theory.

### § 9 The Phlogistonists

The Phlogiston Theory was due in the first place to Becher. Geber (about 776) had taught that all combustible substances burned because they contained the "principle of inflammability," and he identified this principle with sulphur. Becher (1667) pointed out that many combustible substances were known which did not contain sulphur and postulated instead the presence of another principle which he termed *terra pinguis*.

This idea was extended by Stahl (1660-1734) in whose hands the *terra pinguis* of Becher became phlogiston (from the Greek *φλογίστω*, I set on fire). According to this theory the conversion of a metal into its calx\* was due to escape of phlogiston or

$$\text{Metal} - \text{phlogiston} = \text{calx}.$$

Accordingly, in order to regenerate the metal it must be acted upon by a substance rich in phlogiston. Carbon, on account of its ready combustibility and the small amount of residue left on heating, was thought to be rich in phlogiston; hence the reconversion of a calx into the metal by heating with carbon is readily explained. In a similar way a great many of the then known facts of chemistry could be explained and co-ordinated and, in fact, if we replace "presence of phlogiston" by absence of oxygen, the explanations of the Phlogiston Theory become true. The theory ultimately broke down when it was quantitatively tested—its final overthrow being due to Lavoisier (see Chapter 26), but it had certain defects from the beginning. It failed really to account for the fact that air is necessary for combustion, although an attempt was made to obviate this difficulty by the suggestion that something was necessary to take up the escaping phlogiston. Also the fact which had been known to J. Rey in 1630, that a calx is heavier than the metal from which it is made, could only be explained by the phlogistonists by the improbable assumption that phlogiston possessed negative weight!

The Phlogiston Theory is sometimes held up to ridicule, but this is unfair both to the theory and to the men who upheld it. It represented the most perfect generalization known to the best intellects of its day and under its influence chemistry thrived and multiplied its proportions. It served its purpose for a considerable period, for it

\* The process of heating a metal in air so as to convert it into a calx, is called *calcination*. The calces are generally equivalent to what the modern chemist calls "metallic oxides."

afforded a means, lacking before, of correlating, classifying and explaining an otherwise disconnected series of chemical facts. In due course, when it became clear that it was no longer tenable, it was discarded; but considerable achievements stand to its credit and it affords us an excellent example of the rise and ultimate fall of a theory owing to the discovery (through its aid) of new facts inconsistent with it. It may well be that some of the theories of the present day which are regarded as firmly established may be thought of by posterity as the Phlogiston Theory is now thought of, and *our* inexplicable obtuseness and ignorance may well be a source of amazement to them. This need cause us no embarrassment.

A fallacious theory may be a valuable guide to experiment. Experiment and labour applied to the explication of the most extravagant hypothesis is not always lost. Guided by wrong hypotheses men have sought one thing and found another—Columbus sought the Indies, and discovered America.

### § 10 Chemistry at the End of the Eighteenth Century

The latter part of the eighteenth century was a period in which the number of chemical substances known was enormously extended. The pre-eminent worker of the time in this field was Scheele (1742–1786), an apothecary of Uppsala and Köping in Sweden, who discovered a great many new substances of all types, among which may be mentioned chlorine, hydrofluoric acid, arsenic acid, lactic acid, oxalic acid, citric acid, tartaric acid, tungstic acid and many other substances. He is also entitled to priority by two years in the discovery of oxygen, although, owing to the slowness of publication and dissemination of such results in those days, Priestley may be credited with having discovered it independently.

Priestley (1733–1804) was an assiduous experimenter and a most capable investigator. He is noteworthy for the work on gases which he was able to carry out after perfecting and adding to the apparatus suggested by Stephen Hales (1677–1761) for the manipulation of gases. With the aid of the pneumatic trough and other apparatus which he invented, he discovered, or prepared in a pure state for the first time, many common gases such as oxygen (but see above *re* Scheele), nitric oxide, hydrogen chloride, sulphur dioxide, silicon tetrafluoride, ammonia and nitrous oxide. The discovery of oxygen, which he communicated to Lavoisier, was probably his most important contribution to chemistry, for in the hands of the latter it became the instrument for the final overthrow of the Phlogiston Theory. Priestley himself, however, remained a convinced phlogistonist to the last.

During the last quarter of the eighteenth century important chemical investigations of a quantitative nature were undertaken, notably by Black (1728–1799), Cavendish (1731–1810) and Lavoisier (1743–1794).

The work carried out by Black at Glasgow was instrumental in clearing up the interrelationships of carbon dioxide, chalk and lime, magnesia and magnesium carbonate, and caustic soda and sodium carbonate; and the completeness of the explanations was due to their being based on quantitative data obtained by him. This work is also of importance in that it attracted considerable attention at the time and was thus a means of spreading clearer ideas about the nature of chemical combination than had been current previously.

Cavendish is perhaps most often remembered for his celebrated investigations into the composition of water, which he established on a quantitative basis. The importance of his results in relation to the theory of phlogiston was not altogether realized by him for, like Priestley, he remained a believer in the Phlogiston Theory. His quantitative experimental work was marked by a degree of accuracy remarkable for the period.

A notable example of this is furnished by his experiments on the absorption of air by sparking with addition of oxygen, over a solution of caustic alkali, as a result of which he recorded that he could not bring about the absorption of the last bubble of air, being in amount  $\frac{1}{120}$ th of the whole. He may thus be regarded in one sense as the discoverer of the Inert Gases (see Chapter 26), and it is interesting to note that modern work places the proportion of these gases in the atmosphere at  $\frac{1}{104}$ th part of the whole; the difference is accounted for by the fact that argon is appreciably soluble in water.

To Lavoisier is due the credit of having demonstrated that the Phlogiston Theory was no longer tenable and of suggesting and establishing the true theory of combustion. This work is described in detail in Chapter 26, and is important for its strictly quantitative character.

From the time of Lavoisier the science of chemistry has developed with remarkable rapidity and accuracy, and its subsequent history will be found interwoven in the chapters which follow.

## CHAPTER 2

### THE ATOM

Nil posse creari de nilo.—LUCRETIVS

#### § 1 The Atomic Theory

SPECULATION as to the nature of matter is probably as old as philosophical thinking itself. It is clear that matter must either be capable of infinite subdivision (that is, be continuous) or that the process must reach a point beyond which no further division is possible (that is, that matter is discrete).

Many philosophers have concluded in favour of the latter hypothesis, notably Kanáda (the founder of a system of Hindu philosophy long prior to the rise of the Greek philosophers), Democritus, a Greek of the fifth century B.C., and Lucretius, a Roman of the first century B.C. Such an hypothesis is known as an *atomic* hypothesis and the ultimate particles of matter which it postulates are called atoms (from the Greek *átom*, not, and *τέμνω*, I cut).

Many thinkers of more modern times such as Francis Bacon, René Descartes, Robert Boyle and Isaac Newton in the seventeenth century held some kind of theory of atoms. Newton indeed, tried to explain Boyle's Law on the assumption that gases are made up of small naturally repulsive particles and referred chemical changes to different associations of atoms.

Although it is thus not possible to say who invented the Atomic Theory it was with the work of John Dalton that it became the basis of modern chemistry. Dalton, in 1801, employed the atomic hypothesis to explain the diffusion of gases and later, in 1803, put forward the following postulates which may be regarded as a brief statement of his Atomic Theory:

1. Atoms are real, discrete particles of matter which cannot be subdivided by any known chemical process.
2. Atoms of the same element are identical, especially in weight.
3. Atoms of different elements differ from each other and have different weights.
4. Compounds are formed by the union of atoms of different elements in simple numerical proportions.
5. The combining weights of the elements represent the combining weights of their atoms.

Dalton's Atomic Theory was based upon the results of experiment and it provides a ready explanation for the fundamental Laws of

Chemistry, viz., the Law of Conservation of Mass, the Law of Constant Composition, the Law of Multiple Proportions and the Law of Reciprocal Proportions. It thus stood on a quite different footing from the atomic theories of earlier generations.

The growth of chemistry since the beginning of the nineteenth century has been guided, and dominated, by the Atomic Theory. During the nineteenth century Dalton's ideas prevailed; more modern work has indicated that Dalton's original Theory needs modification in certain respects but, even so, it has remained the basis upon which the subject has developed and is developing.

## § 2 The Structure of the Atom

*General.* The discovery of the electron, in 1895, by J. J. Thomson was the result of investigations into the discharge of electricity through gases. The electron was shown to be an extremely minute particle negatively charged and it is now believed to be the unit of negative electricity having a mass of  $1/1837$  of a hydrogen atom. It was also found that electrons can be obtained from a variety of sources but that from whatever source they are obtained their properties are identical. As a consequence of these results it was concluded that all matter contains electrons and that therefore the different atoms of all the elements must contain electrons since the electron is so much smaller than even the lightest atom (hydrogen). It thus follows that the atom must possess a structure and can no longer be regarded as indivisible by any means whatsoever although it can still be said to be incapable of subdivision by any known chemical process.

The idea that the atoms of the elements are, in fact, made up of simpler particles was implicit in the view put forward by Prout (and known as Prout's hypothesis) in 1816. Prout had suggested that the atoms of all the elements, except hydrogen, were made up of suitable numbers of atoms of hydrogen. This idea was abandoned after increasingly accurate determinations of the atomic weights of the elements (notably by Stas, see page 104) had shown that these weights are not, in general, exact multiples of the atomic weight of hydrogen. In more recent times, Prout's hypothesis has been revived in a different form.

So soon as the atomic weights of the elements had been found with reasonable accuracy many attempts were made to discover some relationship between the atomic weight and the properties of an element. These attempts culminated in the work of Mendeléef and of Lothar Meyer who, independently, came to the conclusion that "the properties of the elements are a periodic function of their atomic weights." This generalization is known as the **Periodic Law** and was summarized by Mendeléef in his **Periodic Table** of the Elements. Here again it is difficult to escape from the idea that the atoms must possess some sort of structure so that elements which exhibit similar properties do so because their atoms are similarly constituted.

All these ideas have received striking confirmation as the result of the investigations which began with the discovery of radioactivity by Berquerel in 1896 and of X-rays (or Röntgen rays) by Röntgen in 1895. As the result of the work begun by Rutherford, Soddy, and Moseley it is now believed that the atoms of all elements are built up of three fundamental sub-atomic particles. These are the electron, the proton, and the neutron. The proton is a particle, believed to result from the removal of an electron from an atom of hydrogen, having approximately the same mass as a hydrogen atom but positively charged; the neutron is essentially similar to the proton but is uncharged. Of recent years physicists have postulated the existence of a number of other sub-atomic particles such as the positron, the neutrino, the meson, etc. These have only a transient existence and are not involved in theories of the structure of the atom from the standpoint of chemistry.

According to present views atoms consist of a central, extremely minute, positively charged **nucleus**, in which almost the entire mass of the atom is concentrated, surrounded by electrons, planet-wise, sufficient in number to make the atom as a whole neutral. The electrons are supposed to occupy orbits defined according to the principles of the Quantum Theory (q.v., page 147) and to be the effective instruments of the chemical behaviour of the atoms. The magnitude of the charge on the nucleus, called the **Atomic Number**, differs from element to element and, as it fixes the number of the planetary electrons, it determines also the chemical properties of the element. Except in the case of hydrogen the magnitude of the charge on the nucleus (the charge on the electron being taken as unity) is, in general, smaller than the atomic weight of the element concerned; it follows that the nucleus is not composed entirely of protons (except that of hydrogen, the atom of which is composed of one proton and one electron) but contains neutrons as well. For example, the nucleus of fluorine, with an atomic weight of 19, has a charge of nine units; it must, therefore, be composed of nine protons and ten neutrons, and the neutral atom of fluorine will have nine planetary electrons in addition.

### Isotopes

The idea that the nucleus of an atom is composed of protons and neutrons provides an explanation of the existence of *Isotopes* (i.e. atoms having the same chemical properties but different masses), first observed through the study of the radio-elements but later shown to occur widely among the common and non-radioactive elements also. The chemical nature of an element depends upon the nuclear positive charge (i.e., only upon the number of protons present in the nucleus of the atom) whereas the atomic weight is equal to the sum of the number of the protons and neutrons present. As the number of neutrons present can vary (between limits) without any variation in the number of protons the occurrence of isotopes naturally follows. For example, the atoms of the element chlorine, with an atomic number of 17, must



contain 17 protons. In fact, two isotopes exist containing 18 and 20 neutrons respectively, corresponding to "atomic weights" or *mass numbers* of 35 and 37. As these occur, roughly, in the proportion of 3 to 1, the observed atomic weight (the average of the weights of a very large number of individual atoms) is about 35.5. The fact that the atoms of a given element are not all identical in weight (although they are identical in atomic *number* and hence in chemical properties) is the most important of the postulates of Dalton's Atomic Theory which are now no longer tenable.

### The Extra-Nuclear Structure

The nuclear charge on the atoms of a given element is a fundamental characteristic of that element and the number of electrons surrounding the nucleus is likewise determined, as has been seen above, by this charge. In order to relate these ideas about atomic structure to the known facts of chemistry three questions need to be answered. These questions are (i) how are the electrons arranged, (ii) how can the arrangements be correlated with the chemical properties of the elements, and (iii) what change takes place in the arrangement of the electrons when a chemical change (in particular, chemical combination) occurs?

The nuclear charge increases by one unit as we pass from a given element to the next in the Periodic System and its value is also known as the Atomic Number of the element. The electrons are situated in orbits or shells (usually referred to by the letters K, L, M, N, O, P, Q) and the number of electrons in any given shell cannot exceed a certain maximum. Classical mechanics are inconsistent both with the stability of such a system as is assumed (the electrons would lose energy continuously, and ultimately, fall into the nucleus) and also with the nature of the radiations observed in the spectra of the elements which would be continuous, and not line spectra. The principles of the Quantum Theory accordingly have been applied to the problem. According to this theory energy cannot be radiated, or absorbed in continuously variable amounts, but only in definite "bundles" or *quanta*, and the application of this idea provides a satisfactory explanation of the observed behaviour and properties of atoms. The Quantum Theory leads to the conclusion that the electrons would arrange themselves in groups (i.e., shells) containing (for the first three groups, for example) 2, 8 and 8 electrons. This is in striking conformity with the reappearance of similar properties among the lighter elements (up to the end of the second Short Period of the Periodic System) at each eighth element, e.g.

He	Li	Be	B	C	N	O	F
Ne	Na	Mg	Al	Si	P	S	Cl

In all the elements the outermost group (or shell) of electrons can never exceed eight in number; this shell of eight electrons has a peculiar stability of great chemical significance: it explains the chemical inertness

of the Inert Gases and is the basis of the theory of valency. Deeper shells in the heavier atoms can contain up to 18 (or even 32) electrons as can be seen from the following table showing the electronic structures of the atoms of the Inert Gases.

Element	At. No.	No. of electrons					
		K	L	M	N	O	P
He	2	2					
Ne	10	2	8				
Ar	18	2	8	8			
Kr	36	2	8	18	8		
Xe	54	2	8	18	18	8	
Rn	86	2	8	18	32	18	8

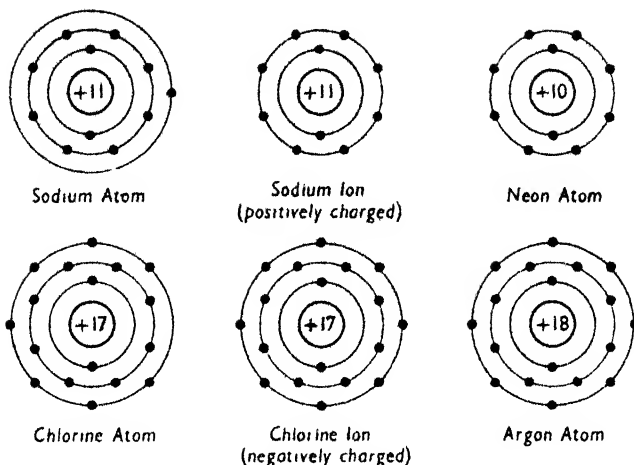
This expansion of shells, deeper in the atom than the outside one, assists in the understanding of the nature of the transition elements and of the Rare Earth elements (see Chapter 11).

### § 3 The Electronic Theory of Valency

The word valency is used in two (albeit closely related) senses, in one of which it is a number which defines the number of units into which the combining power of an element can be divided, and in the other it denotes the fact of combination, or reaction, in general terms.

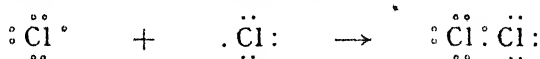
Two types of union, or link, are known called, respectively, electrovalent (or ionic) and covalent. The former occurs in electrolytes (substances which conduct electricity when fused, or in solution), the latter in other compounds or the compound radicals which occur in many ions (e.g., the carbonate or sulphate ions). Electrovalencies are non-directional and the compound (e.g., solid sodium chloride) is held together by the electrostatic attraction between the ions; covalent links are directional and brought about by the sharing of electrons.

An **electrovalency** may be thought of as the result of the complete transfer of an electron from one atom to another; the atom which has lost an electron thus becoming positively charged, the atom which has gained an electron being now negatively charged. The two ions thus formed then hold together by electrostatic attraction. For example, a sodium atom has the electronic structure 2.8.1. If it loses its outermost (or valency) electron an electronic structure identical with an Inert Gas (in this case neon) results. The outermost shell which now contains eight electrons is a particularly stable structure. Hence, the ready formation and stability of the sodium ion. Similarly, a chlorine atom has the electronic structure 2.8.7. By gain of an electron (thereby forming a chlorine ion) the stable Inert Gas structure again results (this time, that of argon). These effects may be illustrated diagrammatically, thus:

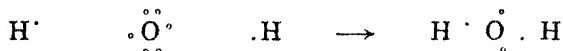


In a **covalent link** two electrons become shared between the atoms which are being joined. Normally, atoms enter into combination thus when each can supply an electron to form a pair in such a way that, after the link is formed, both of the electrons in the pair can participate in the structures of the atoms so united. Electron sharing in this way is a process of electron gaining and the process is subject to the same limit as in the free atoms themselves, that is, normally there can be no more than eight electrons in the outermost shell counting *all* the *shared* electrons.

A simple example of this process can be seen in the formation of a chlorine molecule from two chlorine atoms. The outermost shell of a chlorine atom contains seven electrons; if one of these be shared with a similar one from another chlorine atom in the way described above each atom will then have a share in eight electrons: a stable state. Diagrammatically, this can be illustrated.



Similarly oxygen, with six electrons in the outer (or valency) shell, and hydrogen, with one electron, can combine to form water thus (hydrogen achieving a share in *two* electrons, the maximum for the first, or K shell):

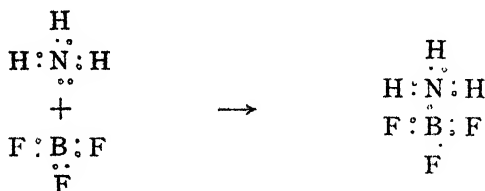


The observed (numerical) valencies of the elements are found, in this way, to be satisfactorily deducible from the electronic structures of the atoms of the elements concerned both in electrovalent and covalent compounds.

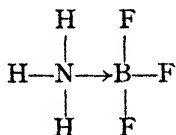
A further type of covalency results when the link is formed by the

supply of *both* the linking electrons by the same atom although in the compound which is formed they are both shared between the two atoms. Such a bond is called a **co-ionic or co-ordinate link**; sometimes the terms dative bond or semi-polar double bond are used.

An example of a co-ionic link is furnished by the compound which is formed from ammonia and boron trifluoride (formulated  $\text{NH}_3 \cdot \text{BF}_3$ ). The nitrogen atom in a molecule of ammonia has eight electrons in its valency shell; three pairs are shared with the hydrogen atoms and one pair is unshared and known as a lone pair. Similarly in a molecule of boron trifluoride there are six shared electrons—two fewer than the eight required for the greatest stability. Ammonia and boron trifluoride therefore combine through the sharing of the lone pair of electrons of the ammonia molecule between the nitrogen and boron atoms which now both have eight electrons in the valency shells.



The atom which provides the pair of electrons in a co-ionic link is often known as the *donor*; that which receives them is, similarly, called the *acceptor*. In ordinary formulation a co-ionic link is, therefore, often represented by an arrow pointing from the donor to the acceptor, e.g.



in the instance quoted.

The sharing of a pair of electrons, in a co-ionic bond, which both came originally from the same atom results in the donor atom acquiring a small positive charge while the acceptor becomes, similarly, slightly negatively charged. This confers a certain degree of polarity on the molecule as a whole which has important consequences in the properties of the resulting compound and provides in turn a means for the detection, experimentally, of the existence of such a link. Thus, for example, a compound which contains a co-ionic link is less volatile (i.e., has a higher boiling point) than an analogous, or isomeric, substance which contains only ordinary covalent links.

#### § 4 Conclusion

It can be seen from the summary given in this chapter that the modern conception of the atom, as being composed of a minute, positively charged nucleus (made up of protons and neutrons) surrounded by electrons in definite orbits or shells, provides a basis for the understanding and explanation of the facts of chemistry. For many purposes, therefore, it can be used as the foundation from which the study of the subject can begin, as will be seen again in later chapters of this book. The whole subject is, however, of such importance that the experimental evidence for this conception, and the way in which it has been accumulated, step by step, needs to be considered. This is done in the chapters which immediately follow.

## CHAPTER 3

# THE PROPERTIES OF GASES

The generality of men are so accustomed to judge of things by their senses that because air is invisible they ascribe but little to it, and think of it as but one remove from nothing.—R. BOYLE (1673).

### § 1 The Gaseous State of Matter

CHEMISTRY (page 4) is concerned with the composition and properties of the different kinds of *matter* in the Universe . . . and the study of matter has led to the recognition of three states of matter, viz., the solid, the liquid, and the gaseous.

The third of these states of matter—the gaseous—was formally recognized by J. B. van Helmont, early in the seventeenth century, and it has been said that the discovery might have slipped back into oblivion had it not been emphasized by the invention of a name—**gas**—which he derived from the *chaos* of the ancients. Some, however, have sought to derive the word from the *geist* (spirit) of the German.

A gas is usually defined by saying that it will occupy the whole of the space available to it.

### § 2 The Influence of Pressure on the Volumes of Gases—Boyle's Law

Robert Boyle having observed in the course of some experiments that a partially inflated lamb's bladder, placed under the receiver of an air pump, became distended when the air was exhausted from the receiver, was led to study the behaviour of air under different pressures.

He investigated the subject quantitatively by means of a U-tube of uniform bore having the shorter leg hermetically sealed at one end and the end of the longer leg open. He poured mercury into the longer leg so as to fill the bend and reach to the same height in both legs, thus confining a sample of air under a pressure equal to that of the atmosphere. He measured the length of the air space and then poured successive portions of mercury in the open end of the tube. After each addition of mercury he measured the length of the air space, and the difference between the levels of the mercury in the two limbs of the tube. In a tube of uniform bore, the length of the air space is proportional to the volume of the air contained in it, and Boyle was thus able to determine the relation between the volume of a given portion of air and the pressure to which it was subjected, as measured by the difference in level between the two mercury surfaces.

Boyle thus found (1661) "the pressures and expansions," as he expressed it, "to be in reciprocal proportions." In other words, **the volume of a fixed mass of gas varies inversely as the pressure to which it is subjected provided that the temperature is kept constant.** This is **Boyle's Law.** E. Mariotte, fourteen years after Boyle's publication, followed along the same lines, and, on the Continent, the law is sometimes improperly ascribed to Mariotte.

Boyle showed further, by means of an arrangement similar to that illustrated in Fig. 3.1, that this same generalization holds good at pressures less than atmospheric. Some mercury is poured into a narrow tube which is closed at one end and open at the other. The tube is inverted in the tall cylinder of mercury. The narrow tube is raised or lowered, and the volume of gas confined in the narrow tube and the difference in the level of the mercury in the narrow and in the wider tube, are read at the same time. The pressure on the mercury in the wide cylinder is one atmosphere, and the pressure of the gas in the narrow tube is one atmosphere less the pressure of a column of mercury equal to the difference in the level of the mercury in the two tubes.

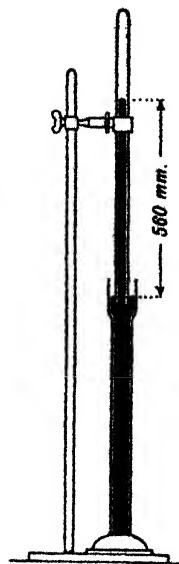


FIG 3.1.  
Boyle's Law—  
Low Pressures

If  $p$  be the pressure on a given mass of gas when its volume is  $v$ , then, at a constant temperature, it follows from Boyle's Law that

$$p \propto \frac{1}{v}$$

$$\text{i.e., } p = \frac{k}{v} \text{ (where } k \text{ is a constant)}$$

$$\therefore pv = \text{Constant.}$$

Hence it follows that the behaviour of a gas which is represented by Boyle's Law is graphically expressed by a rectangular hyperbola (see Fig. 3.2—unbroken curve).

### § 3 Deviations from Boyle's Law

The pressures used by Boyle extended over a range varying from 3 cm. to 300 cm. of mercury. It is hazardous to infer that because the product  $pv$  is constant over a limited range of pressures, it will remain constant for pressures widely different from those actually measured. Many careful investigations have since been made, notably by Amagat, to find if the simple law of Boyle correctly describes the behaviour of gases at pressures far removed from the normal pressure of the atmosphere—76 cm. of mercury. The results show that no two gases behave

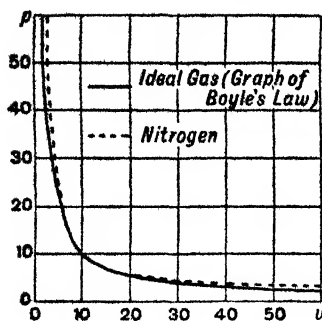


FIG. 3.2.  
Volume-pressure curves

$p$	1	50	100	125	150	200	500	1000 atm.
$p v$	1	0.92	0.49	0.31	0.41	0.50	1.02	1.81

that is, the product  $p v$  at first diminishes in magnitude and then steadily increases, as is brought out very clearly by plotting the numbers on a graph. If the products  $p v$  were constant for all values of  $p$  we should get the straight line, dotted, and marked "ideal gas" in Fig. 3.3; with carbon dioxide, however, the curve descends below the line for an ideal gas, and then steadily rises, passing above the ideal gas line when the pressure is nearly 500 atmospheres.

The curves for hydrogen and helium, at ordinary temperatures, do not descend below the ideal gas line, but take a path resembling the hydrogen line shown in Fig. 3.3. However, even these gases exhibit the same peculiar behaviour at lower temperatures. Thus, with hydrogen at  $-140^\circ$ , the product  $p v$  reaches a minimum when the pressure is about 25 atmospheres; at  $-195^\circ$ , 45 atmospheres; and at  $-213^\circ$ , 51 atmospheres.

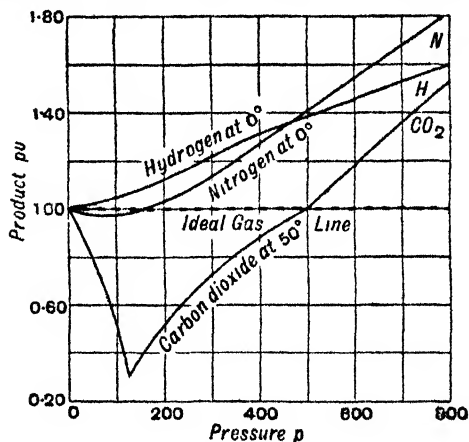


FIG. 3.3.—Pressure- $p v$  curves (Amagat).

in precisely the same way. The deviations for many gases are insignificant. Boyle's law, when graphed, furnishes the continuous curve shown in Fig. 3.2. This continuous curve is a rectangular hyperbola. The deviations of nitrogen, for example, from this ideal condition are indicated by the dotted line.

E. H. Amagat (1893) showed that while the product  $p v$  remains fairly constant at low pressures for many gases, the numerical value of  $p v$  changes in a remarkable manner as the pressures increase in magnitude. Amagat's measurements for carbon dioxide show that when



#### § 4 Influence of Temperature on the Volumes of Gases— Charles's Law

In 1790, Joseph Priestley concluded "from a very coarse experiment" that "fixed and common air expanded alike with the same degree of heat," and J. L. Gay-Lussac, in 1802, quoted some experiments in support of the broader view: **The volume of a given mass of all gases increases by  $\frac{1}{273}$  of its volume at 0° C. for every degree Centigrade rise in temperature.** This law is designated **Charles's Law**, in honour of J. A. C. Charles, who, according to Gay-Lussac, made some crude experiments on the subject fifteen years before Gay-Lussac's publication. Some call this relation "Gay-Lussac's Law."

The increase in volume which occurs when one litre of nitrogen at 0° is heated in a suitable vessel is shown in Table I (R. Chappius, 1888):

TABLE I—COEFFICIENTS OF THERMAL EXPANSION OF NITROGEN

Temperature °C.	Volume in litres	Expansion per litre per degree
0	1.0000000	
10	1.0367781	0.0036778
20	1.0735396	0.0036770
30	1.1102875	0.0036762
40	1.1470244	0.0036761

The numbers in the last column—called **the coefficients of thermal expansion**—mean that the volume  $v$  of a litre of nitrogen, measured at 0°, when heated through  $\theta$ °, can be represented very closely by the expression:  $v = (1 + 0.003676 \theta)$  litres. In other words, nitrogen increases 0.003676, or very nearly  $\frac{1}{273}$ rd of its volume at 0° for every degree rise of temperature. More generally, if  $v_0$  be used to denote the volume of a gas at 0°, we have

$$v = v_0 \left( 1 + \frac{\theta}{273} \right)$$

This is very nearly true for most of the common gases, for while solids and liquids have their own characteristic coefficient of expansion, gases have nearly the same coefficient of thermal expansion. This is the meaning of Charles's Law. The coefficients for the gases run something like this:

Air	.	.	.	.	.	.	0.003665
Hydrogen	.	.	.	.	.	.	0.003667
Carbon dioxide	.	.	.	.	.	.	0.003688

These numbers are close enough to  $\frac{1}{273}$  ( $= 0.003663$ ) for most practical purposes. In general, the more easily a gas is liquefied, the greater the deviation from the constant 0.003665 found for air—witness carbon dioxide.

By plotting the above equation, we get a straight line which cuts the  $T$  axis at  $-273^\circ$  (see Fig. 3.4). If the temperature were less than  $-273^\circ$ , the gas would have a negative volume, that is a volume less than nothing! If the temperature were exactly  $-273^\circ$ , the gas would occupy no volume! It is impossible to imagine a substance occupying no space, but this seems to be a logical conclusion from Charles's Law.

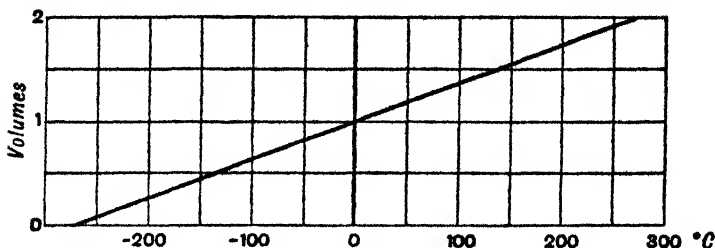


FIG. 3.4 —Graph of Charles's Law

Where is the fallacy? Charles's Law includes a simplifying assumption. The apparent volume of a gas may be resolved into at least two parts: (1) the "volume" occupied by the molecules of the gas; and (2) the space between the molecules. Although, for the sake of simplicity, we assume  $v$  is employed to represent the *total volume* occupied by the gas, in reality  $v$  should refer only to the space between the molecules, and in that case, the conclusion that  $v = 0$  when the temperature is  $-273^\circ$  involves no absurdity. Moreover the gas would liquefy before the temperature  $-273^\circ$  was attained, and the simple gas law of Charles would not then be applicable.

The temperature  $-273^\circ \text{C.}$  is consequently supposed to be a limiting temperature—the nadir or lowest possible temperature. Hence, it is sometimes called the **absolute zero**; and temperatures reckoned from this zero are called **absolute temperatures**. Several other distinct lines of inquiry converge to this same absolute zero. On the absolute scale of temperatures,  $0^\circ \text{C.}$  will be  $273^\circ \text{abs.}$  If  $T$  be employed to denote the temperature on the absolute scale, and  $\theta$  the temperature on the centigrade scale, we have  $T = 273 + \theta$ . Hence, we see that if  $v$  be the volume of a gas when the absolute temperature is  $T$ , and  $v_1$  the volume when the temperature is  $T_1$ , we get, from the preceding equation, another way of stating Charles's Law:

$$\frac{v}{T} = \frac{v_1}{T_1}$$

### § 5 Deviations from Charles's Law

As has been pointed out already, the coefficients of thermal expansion of all gases are only approximately the same. The coefficients for the individual gases differ a little among themselves as indicated above.

The variation in the coefficient of thermal expansion at temperatures and pressures not far removed from normal atmospheric temperatures and pressures is not very marked, and for simple gas calculations can be ignored. It remains to indicate the variation, if any, in the coefficient of thermal expansion with large variations of temperature and pressure.

1. *The influence of pressure.*—The coefficient of expansion of most gases is increased by augmenting the pressure of a gas until a maximum value is attained, after that the coefficient diminishes with increased pressure. For instance, E. H. Amagat (1893) found that the coefficients of expansion of carbon dioxide at temperatures between 50° and 60° assumed the following values:

Pressure	30	60	125	200	500	1000 metres of mercury
Coefficients	0.0069	0.0085	0.0410	0.0085	0.0033	0.0018

Carbon dioxide thus shows a marked variation in the coefficient of thermal expansion at high pressures. The coefficient also diminishes as the pressure is reduced. The variation is not so marked with gases like nitrogen, oxygen and hydrogen, which are not easily condensed to the liquid condition. The value of  $p$  which furnishes the greatest coefficient of thermal expansion is that same value of  $p$  which gives the minimum product  $pv$ , page 22. At ordinary temperatures, therefore, hydrogen and helium do not exhibit this variation in the value of their coefficients of expansion, and the coefficient of expansion steadily diminishes with increasing pressure.

2. *The influence of temperature.*—The maximum value for the coefficient of expansion with increasing pressure just indicated becomes less and less as the temperature is raised and finally disappears. So does the minimum value of the product  $pv$  become less and less marked as the temperature is raised. The gradual "flattening" of the carbon dioxide curves as the temperature rises from 40° to 100° is brought out very clearly in Fig. 3.5. We have seen, page 24, that all gases exhibit a minimum value for  $pv$ . The pressure required for the minimum depends on the temperature as well as on the nature of the gas. The minimum is most marked when the gas is near its critical temperature (page 44). If the temperature is much above the critical temperature, the minimum is very small—with hydrogen the minimum is inappreciable at 0° (Fig. 3.4). All other gases show a minimum at ordinary temperatures. Hence, Regnault, who discovered this phenomenon, was led to say that hydrogen is a "*gaz plus que parfait*." But hydrogen also shows the minimum at reduced temperatures as indicated on page 22.

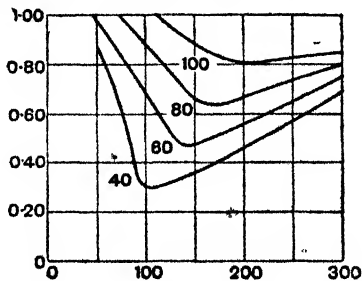


FIG. 3.5.—Amagat's Curves for Carbon Dioxide

### § 6 The General Gas Equation

Boyle's Law, expressed mathematically in the form  $p v = \text{Constant}$ , and Charles's Law, which may similarly be expressed in the form  $v/T = \text{Constant}$ , when combined into one equation give us a mathematical expression for the variation in the volume of a gas when temperature and pressure both vary. This combined equation is

$$\frac{p v}{T} = \text{Constant.}$$

In this expression, when the quantity of gas concerned is a gram-molecule (see page 84), the constant is usually denoted by  $R$  and called the **gas constant**, so that the equation becomes

$$p v = R T,$$

when it is known as the **General Gas Equation**.

In the form

$$\frac{p v}{T} = \text{Constant,}$$

this equation is frequently employed in calculations involving variations in the volumes of gases due to changes in temperature and pressure. Thus, the volume is often determined at the temperature of the laboratory and at a pressure not equal to the standard pressure, whereas for chemical purposes it is usually necessary to know the volume at **standard (or normal) temperature and pressure**, that is, at  $0^\circ \text{C.}$  and 760 mm. pressure; conditions which are often referred to by the abbreviations S.T.P. or N.T.P.

If  $p$ ,  $v$  and  $T$  respectively denote the pressure, volume and absolute temperature of a given mass of gas under one set of conditions, and  $p_1$ ,  $v_1$  and  $T_1$  the pressure, volume and absolute temperature under another set of conditions, then from the above expression,

$$\frac{p v}{T} = \frac{p_1 v_1}{T_1}$$

As an example suppose that a gas measures 170 c.c. at a pressure of 735 mm. of mercury and at a temperature of  $15^\circ \text{C.}$ , and that it is required to find its volume at standard temperature and pressure. We then have  $p = 760$ ,  $T = 273$ ,  $T_1 = 288$ ,  $v_1 = 170$  and  $p_1 = 735$ , while  $v$  is the volume required. Hence

$$\begin{aligned} \frac{760 \times v}{273} &= \frac{735 \times 170}{288} \\ \therefore v &= \frac{735 \times 170 \times 273}{288 \times 760} = 155.8 \text{ c.c.} \end{aligned}$$

### § 7 Dalton's Law of Partial Pressures

When two gases which do not act chemically on one another under the conditions of the experiment are brought together they mix intimately, by diffusion (page 31), so as to form a homogeneous mixture, and John Dalton (1802) found that in such a case each gas seemed to exert the same pressure as if it alone occupied the space; the total pressure of the mixture of gases being the sum of the several pressures due to each gaseous component of the mixture. That is, if  $P$  be employed to denote the total pressure of the mixture,  $p_1$  the partial pressure exerted by one of the gases, and  $p_2$  the partial pressure exerted by the other gas,  $P = p_1 + p_2$ . In words, **in a mixture of gases which exert no physical or chemical action on one another, each gas exerts the same pressure as if it alone occupied the entire vessel, and the total pressure is the sum of the partial pressures due to each gas.** This is Dalton's law of partial pressures. It can be extended to mixtures of any number of gases.

The law only holds strictly for perfect gases. The behaviour of actual gases deviates in greater or less degree from that indicated by Boyle's Law, and furthermore, it is highly probable that the molecules of nearly all gases exert some attractive influence on one another, and the gases will, in consequence of this *physical* action, "deviate" from Dalton's Law to an extent dependent upon the magnitude of the intermolecular attraction. Many mixtures of gases show slight but marked deviations from the law, e.g., carbon dioxide and sulphur dioxide; hydrogen with air and with nitrogen, etc.

Thus, for example, when a given quantity of carbon dioxide at 760 mm. pressure is allowed to expand to twice its volume (at the ordinary temperature) its pressure does not fall quite to 380 mm. but becomes 381.1 mm. If, therefore, a mixture be made of equal volumes of hydrogen and carbon dioxide, both at atmospheric pressure, so that the final volume is twice that of either gas in the first place, the final pressure would be not 760 mm. but 761.1 mm.

A common application of Dalton's Law is the calculation at normal temperature and pressure of the volume of a gas measured when collected over water. At ordinary temperatures, water exerts a considerable vapour pressure, and the space occupied by the gas whose volume has been measured is also occupied by water vapour. Hence, by Dalton's Law, the total pressure exerted (and measured) is equal to the actual pressure of the gas in question plus the pressure of the water vapour present. It follows, therefore, that in carrying out the necessary calculation, the value to be used for the pressure of the gas must be the observed pressure minus the pressure of the water vapour present along with the gas. This value, which is the maximum pressure of water vapour at the temperature of the experiment, is taken from tables (see page 40).

### § 8 The Density of a Gas

The density of a gas or vapour can be expressed in two ways, viz.:

- (i) the *normal* or *absolute density*, which is the weight in grams of 1 litre of the gas measured at 0° C. and 760 mm. pressure;\*
- (ii) the *relative density*, which is the ratio of the weight of a given volume of the gas to the weight of an equal volume of hydrogen, measured and weighed under identical conditions.

The implications of the first of these ways of expressing density are those which concern us here. Relative density and its importance will be discussed later (see page 77).

The determination of the absolute densities of gases with a high degree of accuracy requires experimental skill of a high order and calls for the use of delicate apparatus which includes many refinements.

Three methods are available:

- (i) the Globe (or Regnault's) Method;
- (ii) the Volumeter Method;
- (iii) the Buoyancy (microbalance) Method.

#### *The Globe Method*

In this method, an evacuated globe is weighed, filled at a known pressure and temperature with the gas, and then reweighed. The volume of the globe is then determined by filling it with water and weighing it again.

In order to obtain results of the highest order of accuracy many precautions have to be taken and corrections must be applied for those errors that cannot be entirely eliminated.

The following are the principal precautions and allowances which are necessary:

- (i) the globe must be *absolutely dry*,
- (ii) the gas in the globe should be as nearly as possible at a *temperature of 0° C. and a pressure of 760 mm. of mercury*;
- (iii) to avoid errors caused by condensation of moisture on the outside of the glass globe and to allow for changes in the humidity, temperature and pressure of the air in the balance room, the globe is *counterbalanced against an exactly similar globe* and the two globes are always treated in the same manner,
- (iv) a correction must be applied for the *shrinkage* of the globe when evacuated;
- (v) the results must be corrected for the *latitude and height above sea-level* of the place where the observations are made.

In addition to the above, errors may arise owing to adsorption (that is to say, the formation of a very thin, "condensed" layer) of the gas on the walls of the globe. This tends to make the results too high, but with the permanent gases the effect is very small.

The amount of the correction to be applied for the shrinkage of the globe on evacuation is determined as follows. The globe is mounted inside a closed vessel with its stem passing through one of two holes in the stopper of the vessel. A calibrated, vertical capillary tube is fixed into the other hole and the vessel is filled with water and immersed in a constant-temperature bath. The globe is then evacuated and the extent of the fall of the water-level in the capillary tube is observed, from which the amount of the contraction of the globe can be calculated.

\* For the most accurate work the weights must be corrected to sea-level at altitude 45°.

In order to correct for latitude and height above sea-level the value for the density calculated and corrected as above must be divided by

$$(1 - 0.0026 \cos 2\lambda - 0.000000196 h)$$

where  $\lambda$  = latitude of the place of observation  
and  $h$  = height of the place of observation  
above sea-level (in metres).

Notable examples of the use of this method are furnished by the work of Lord Rayleigh on the densities of the common permanent gases (cf. pages 102, 588) and of Morley (1895) on the densities of hydrogen and oxygen.

### *The Volumeter Method*

In this method, the weight of gas, whose volume, temperature and pressure have been measured, is determined either by releasing the gas from an apparatus which delivers only pure, dry gas (e.g., hydrogen absorbed in palladium may be driven off by heating) or by absorbing the gas in a suitable absorbent and determining the increase in weight of the absorption apparatus. A convenient absorbent is charcoal, contained in a bulb immersed in liquid air.

The volumeter method permits the use of large quantities of gas, since the apparatus used for measuring the volume does not require to be weighed and therefore need not be portable, nor restricted to such dimensions as enable it to be attached to a balance.

This method was employed by Guye and Pintza for determining the density of nitrogen and may be understood from Fig. 3.6, which shows their apparatus in a simplified form.

The apparatus consisted of two globes, *A* and *B*, attached to a manometer *D*, to a tube *H* containing coconut charcoal, to a pump and to a source of the gas under examination by means of tubing and suitably disposed glass taps. The volumes of *A* and *B* were determined by finding the weight of water filling them at 0°. The volume of the "dead-space" between *a* and *b* and the tap *G* and the zero of the manometer were also found. The tube *H* (actually attached to the apparatus by a ground joint) was evacuated and weighed. The whole apparatus was then evacuated and the gas whose density was to be found was allowed to enter slowly until the pressure in the apparatus was approximately that of the atmosphere. *A* and *B* were then immersed in melting ice, *F* and *G* were closed, the manometer adjusted to the zero mark and the pressure of the gas was then read. *EFG* was next evacuated, *F* was closed, *E*, *G* and *J* were opened, *H* was cooled in liquid air and so the gas was practically all absorbed in *H*. Taps *E* and *G* were then closed and the pressure of residual gas measured. The gas contained in the space *EFG* was pumped out and measured, while *H* was removed and reweighed. The weight of gas absorbed was thus known, and from the difference in pressure before and after the experiment, and the amount of gas in the "dead-space," the volume of the gas absorbed could be calculated, and hence the density.

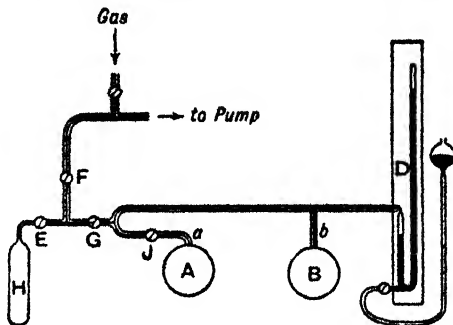


FIG. 3.6.—Guye and Pins'tza  
Volumeter Method

### The Buoyancy Method

This method, which employs a microbalance, depends upon measurement of the pressure of the gas when buoying up a small quartz bulb immersed in the gas, by a fixed amount.

The microbalance used by Lambert and Phillips (1950) was constructed entirely of fused quartz. It is shown diagrammatically in Fig. 3.7. The buoyancy bulb *A* is suspended from one end of the beam by a hook formed at the end of a very fine fused quartz film which is drawn from a point in line with the main axis of the beam; this makes it possible to adjust the zero point (and thus enables pressure ratios to be determined at more than one density) by the addition of quartz riders to the hook from which the buoyancy bulb is hung.

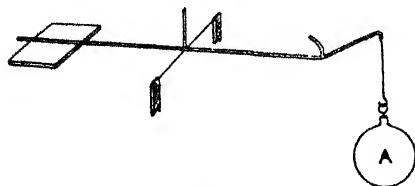


FIG. 3.7. Microbalance

A counterpoise is sealed on a peg situated at the other end of the beam as shown. It is constructed from very thin-walled quartz tubing about 15 mm. in diameter and is formed into a rectangular shape so as to produce the maximum damping effect. The surface area of the counterpoise is arranged to be the same as that of the buoyancy bulb which is evacuated and sealed. The beam is fixed to the framework by stretched quartz fibres,

*DD*, on which it swings. The whole is enclosed in a tube which can be evacuated and the gas is then allowed to enter slowly until the pointer on the end of the beam is exactly level with the one on the framework. The pressure of the gas is measured, and the process is exactly repeated with oxygen.

Let  $v_1$  = volume of the apparatus  
 $p_1$  = pressure of the first gas  
 $p_2$  = " " " second gas (oxygen)  
 $\rho_1$  = normal density of the first gas  
 $\rho_2$  = " " " second gas

If  $w$  is the weight of the first gas, which fills the apparatus at pressure  $p_1$ , then the weight of the second gas which would fill it at the same pressure would be  $w \cdot \frac{p_1}{p_2}$ . It now the pressure of the second gas be altered so that the buoyancy is the same as that of the first gas at a pressure  $p_1$  (i.e., so that the weight of volume  $v_1$  of the gas becomes equal to  $w$ ) the total volume of this weight of gas will become  $v_2 \cdot \frac{p_2}{p_1}$ .

$$\therefore p_1 v_1 = p_2 \cdot v_2 \cdot \frac{p_2}{p_1} \text{ whence } \frac{p_1}{p_2} = \frac{p_2}{p_1}$$

whence the unknown density of the gas under examination can be calculated from the known density of oxygen.

The method is valuable since it is capable of great precision, it requires only a small amount of gas, and can be carried out relatively quickly. Low pressures are employed, for under these conditions Boyle's Law may be considered to express accurately the behaviour of the gases.

The determination of the densities of gases with a high degree of accuracy finds an important application in the evaluation of atomic weights: by furnishing a check on values obtained by purely chemical methods when these are possible; by furnishing one of the few available



physical means for determining these constants when, as in the case of the inert gases, chemical methods are not available. Further details of the method will be given later (see page 111).

### § 9 The Diffusion of Gases—Graham's Law

If a jar of a gas of low density, such as hydrogen, be inverted over another jar containing a much denser gas, like carbon dioxide, it might perhaps be expected that the samples of the two gases would maintain their relative positions, at any rate for some considerable time. In point of fact the two gases—hydrogen and carbon dioxide—will spread throughout the two vessels in a short time and in such a way that the two cylinders will enclose a homogeneous mixture of carbon dioxide and hydrogen. This phenomenon is known as **diffusion** and is closely related to the behaviour of a gas which, when confined in a vessel under a pressure, is allowed to escape through a small orifice. This latter process is called **effusion**.

Doberciner observed in 1823 that hydrogen, collected over water in a cracked flask, escaped into the surrounding air and that the water rose in the neck of the flask. This observation indicates that gases diffuse at different rates and these facts may be demonstrated qualitatively by means of the following experiments.

Porous pots containing air are fixed to the ends of bent tubes as shown in Figs. 3.8 and 3.9. A cylinder of hydrogen is brought over one porous pot, Fig. 3.8. Hydrogen diffuses through the walls of the pot faster than the air can diffuse outwards. Consequently, the pressure of the gas inside the porous pot will increase. This is shown by the motion of the coloured liquid in the U-tube away from the porous pot. Before the cylinder of hydrogen was placed over the porous pot, the air diffused inwards and outwards through the pot at the same rate. Repeating the experiment, Fig. 3.9, with a cylinder of carbon dioxide instead of hydrogen, the air moves outwards from the porous pot faster than the carbon dioxide can pass inwards. Consequently, there is a reduction in the pressure of the gases in the porous pot. This is shown by the motion of the liquid in the U-tube towards the porous pot.

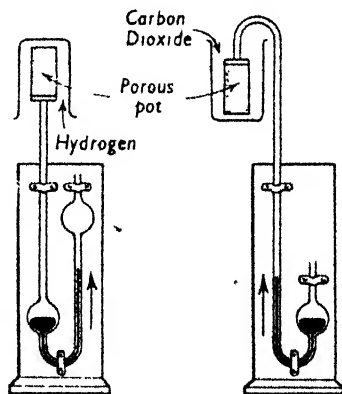


FIG 3.8.

FIG. 3.9.

Diffusion Experiments

The ready diffusion of gas through the walls of buildings plays a part in ventilation. Most building materials are porous, and permit the passage of gases through them in both directions. This is indicated by

the appearance of the ceilings, constructed of lath and plaster on joists, in a room which has not been recently decorated. The ceiling is much more discoloured (on account of dust and smoke particles being filtered out of diffusing warm air) in between the joists and laths than in the places where the laths and joists occur so that the pattern of the construction becomes plainly visible. The diffusion does not take place so readily when the walls are saturated with moisture—e.g., in new buildings.

The quantitative aspect of diffusion was investigated by Thomas Graham (1832). His measurements were made in a series of experiments in which narrow tubes of from 6 to 12 inches in length were closed at one end by means of thin, porous plugs of plaster of Paris. (In some later experiments tubes with a bulb in the middle were employed.) These were filled with the gas under examination and confined over water (or other suitable liquid according to the nature of the gas being investigated) and diffusion allowed to take place. After the lapse of a given time, the gas remaining in the tube was analysed in order to determine the amount of gas remaining and the amount of air which had entered by diffusion. From the results of these experiments, Graham was able to show that the speed at which a gas can diffuse or travel through a thin porous membrane is related to the density of the gas.

TABLE II—SPEEDS OF DIFFUSION OF SOME GASES AND GRAHAM'S LAW

Gas	Relative density (Hydrogen = 1)	Calculated speed of diffusion from 1	Observed speed of diffusion (Hydrogen = 1)
		$\frac{1}{\sqrt{\text{relative density}}}$	
Hydrogen . . . . .	1	1	1
Methane (CH <sub>4</sub> ) . . . . .	8	0.354	0.351
Carbon monoxide (CO) . . . . .	14	0.267	0.278
Nitrogen . . . . .	14	0.267	0.265
Oxygen . . . . .	16	0.250	0.248
Carbon dioxide (CO <sub>2</sub> ) . . . . .	22	0.213	0.212

For example, under similar conditions, hydrogen diffuses nearly four times as fast as oxygen; the relative densities of hydrogen and oxygen are nearly as 1 : 16; and the relative rates of diffusion of the two gases are nearly as  $\sqrt{16} : \sqrt{1}$ ; i.e., as 4 : 1. Thus we have **Graham's Law of diffusion: under comparable conditions the relative speeds of diffusion of gases are inversely proportional to the square roots of their relative densities.** Graham measured the speed of diffusion of gases through thin porous plates, and found the numbers indicated in the last column of the subjoined table recalculated to hydrogen = 1 instead of air = 1 (Table II). The preceding column represents the theoretical numbers calculated on the assumption that the speeds of diffusion

are inversely as the square roots of the relative densities. The observed numbers for the speeds of diffusion agree very closely with those obtained by calculation.

A method for comparing the rates of diffusion of gases is indicated diagrammatically in Fig. 3.10.

A small chamber, *A*, is made at one end of a wide glass tube, *B*, by means of a cork at the top, through which pass two glass tubes as shown, and a porous plug, *C*, at the bottom. The wide glass tube is partly filled with mercury and arranged to stand in another vessel, *D*, containing mercury as indicated; that is, in such a way that the pressure in the wide glass tube below the porous plug is less than that of the atmosphere. A steady stream of gas under atmospheric pressure is passed through the chamber *A* and the wide glass tube is raised gradually so that the difference in level of the mercury inside and outside of *B* is kept constant. The time taken for the mercury surface to pass thus from the mark *E* to the mark *F* is noted. The process is then repeated with another gas (at the same temperature and with the same difference of pressure).

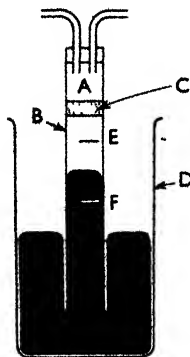


FIG. 3.10.  
Apparatus for comparing Rates of Diffusion of Gases

Since Graham's Law also applies to effusion another convenient method for comparing the densities of gases is by measuring their relative rates of effusion. This can be done by means of the apparatus shown in Fig. 3.11 devised by Bunsen.

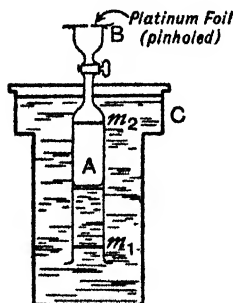


FIG. 3.11

It consists of a tube, *A*, open at the lower end, closed at the other end by means of a tap above which is another short tube across the mouth of which is sealed a piece of platinum foil. This foil is pierced by a very fine aperture. *A* is immersed as shown in a vessel of water, *C*. One of the gases whose rate of effusion is to be compared is forced into *A* until the water level in the tube has been depressed below the lower mark *m*<sub>1</sub>. The tap is then opened and the gas allowed to effuse under the pressure of the displaced water. The time taken for the water-level in *A* to rise from *m*<sub>1</sub> to *m*<sub>2</sub> is measured by a stop-watch. The experiment is then repeated with the other gas.

Then if *t*<sub>1</sub> and *t*<sub>2</sub> are the times required for equal volumes (*v*) of the two gases to effuse, and *r*<sub>1</sub> and *r*<sub>2</sub> are their respective rates of effusion

$$r_1 = \frac{v}{t_1}, \quad r_2 = \frac{v}{t_2}, \quad \therefore \frac{r_1}{r_2} = \frac{t_2}{t_1}$$

But, by Graham's Law,  $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$  where  $d_1$  and  $d_2$  are the densities of the two gases. Therefore  $\frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}}$

### § 10 Applications of Graham's Law

Two practical applications of Graham's Law have been made:

- (1) for the separation of mixed gases;
- (2) for the determination of the density of gases.

If a slow current of a mixture of two gases of different densities be passed through a porous tube, the lighter gas will diffuse through the walls of the tube more rapidly than the heavier. Thus, for example, if a slow current of electrolytic gas, that is, the mixture of hydrogen and oxygen obtained by the electrolysis of water, be allowed to pass through the stem of a "churchwarden" clay pipe, and the gas issuing from the pipe be collected in a gas trough, the gas thus collected will no longer explode when brought in contact with a flame. On the contrary, it will rekindle a glowing chip of wood, showing that a high proportion of oxygen is present. This phenomenon—the separation of one gas from another by diffusion—has been called, by Graham, **atmolyis**, ἀτμός (*atmos*), vapour; λύω (*lyo*), I loosen.

This method has been successfully applied to the separation of the isotopes of neon (see page 141). The densities of these two isotopes are 10 and 11 respectively (compared to hydrogen), so that their rates of diffusion are as  $\frac{1}{\sqrt{10}} : \frac{1}{\sqrt{11}} = 1.0 : 0.953$ . The separation is therefore only slight and it is necessary to repeat the process many times to obtain an appreciable separation. The method was also used for the separation of the isotopes of uranium for use in the first atomic bomb (page 169).

The application of Graham's Law was made use of by Soret (1868) in determining the density of ozone (see page 352). Ladenburg later (1898) having obtained a gas containing 86.16 per cent of ozone determined its density by comparing its rate of effusion with that of oxygen. The value 1.456 for the density of ozone compared to oxygen was obtained.

### § 11 The Kinetic Theory of Gases

The properties of gases and the laws describing their behaviour when the conditions to which they are subjected are altered have so far been discussed from the purely experimental standpoint, and the laws concerned have been arrived at mainly as a result of inductive reasoning based upon the facts provided by experiment. It is now necessary

to consider what hypothesis or theory can be employed to bring these laws into relation with each other.

It is evident that matter must be either a discrete or a continuous medium. The conclusion (cf. Chapter 2) that matter is not continuous is confirmed by the study of diffusion in solids, liquids and gases, for how can two continuous media occupy the same space at the same time? The study of the compressibility of gases—Boyle's Law—leads to the same view. How can a continuous medium on rarefaction (that is, diminution of pressure) expand indefinitely? How can compression diminish the volume of matter itself? If matter be discrete these queries are readily answered. Compression involves a closer packing or a crowding together of the particles by diminishing the space between them.

Conversely, rarefaction involves an increase of the space between them, so that they become less closely packed and less crowded together. If matter be discrete it is easy to understand how one substance can diffuse into another—e.g., hydrogen into air.

A study of the physical and the chemical properties of matter has thus led to one conclusion. **Matter is discrete, not continuous; and it is made up of minute particles called molecules.** This hypothesis is called the molecular theory of matter.

Are the molecules stationary or in motion? Here again the phenomenon of diffusion has led to the assumption that the molecules are in rapid motion. How could gases diffuse one into the other in such a remarkable way if the molecules were at rest? Diffusion and the fact that a mixture of gases with different densities shows no signs of settling compel us to assume that the molecules are in a state of incessant motion, and that they are travelling in all directions.

They seem to lead a more or less independent existence. They appear to be continually moving with a great velocity in sensibly straight lines in all directions. The molecules in their travels must be continually colliding with one another and bombarding the walls of the containing vessel. Thus the molecules continually change their speed and direction.

It is clear that an outward pressure must be exerted on the sides of the vessel every time a molecule strikes the boundary walls. The moving molecules must be perfectly elastic so that after each collision they rebound with the same velocity as before; otherwise, their momentum would decrease with each collision, and the pressure of a gas would decrease with time, which it does not. Hence, it is inferred that **the molecules are in a state of perpetual motion.**

This description of the probable nature of gases is known as the *Kinetic Theory of Gases* and its principal assumptions may be summarized as follows:

- (i) the particles or molecules comprising a gas are in a state of perpetual motion;
- (ii) these molecules move in all directions in straight lines;

(iii) the molecules are continually colliding with each other and with the walls of the vessel in which the gas is confined so that they are constantly changing their speed and direction;

(iv) these collisions are perfectly elastic so that no energy is lost.

## § 12 Deduction of the Gas Laws from the Kinetic Theory

On the basis of the above assumptions and two further ones, viz.:

(a) that the molecules of a gas are of negligible size in comparison with the space they occupy;

and (b) that the molecules do not exert any attraction on each other;

it is possible to make some important deductions.

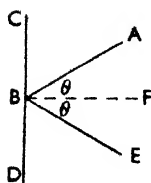


FIG 3.12

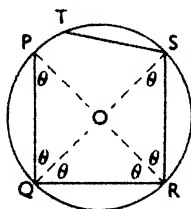


FIG 3.13

Consider first a perfectly elastic particle moving with velocity  $u$  in the direction  $AB$  (Fig. 3.12) and which collides with, and rebounds from, a surface  $CBD$  along the path  $BE$ . Let  $BF$  be the normal at the point of impact and the angle  $ABF$  (which is equal to the angle  $FBE$  since the collision is perfectly elastic) be  $\theta$ . The momentum of the particle can be resolved in two directions, viz., parallel to, and at right angles to,  $CBD$ . The momentum of the particle before collision is then  $mu \sin \theta$  (where  $m$  is the mass of the particle) in

the direction  $CBD$  and  $mu \cos \theta$  in the direction  $FB$ . After collision the resolved portions of the momentum are, similarly,  $mu \sin \theta$  in the direction  $CBD$  and  $mu \cos \theta$  in the direction  $BF$ . That is to say, there has been no change of momentum parallel to the surface  $CBD$ , but in the direction perpendicular to the surface there has been a change of momentum of  $2 mu \cos \theta$ .

Now consider a gas molecule, moving with velocity  $u$ , inside a sphere of radius  $r$ , along the path  $PQRST$  (Fig. 3.13). The distance travelled by the molecule between two consecutive collisions with the wall of the sphere will then be  $2r \cos \theta$ ; a single molecule will, consequently, make  $\frac{u}{2r \cos \theta}$  impacts per second. As shown above, the change of momentum at each impact will be  $2 mu \cos \theta$  and the total change of momentum of the molecule, per second, will be

$$2 mu \cos \theta \frac{u}{2r \cos \theta} = \frac{mu^2}{r}$$

If there be a large number of molecules, confined in the sphere, moving with velocities  $u_1, u_2, u_3, \dots, u_n$  then the total change in the momentum of all the molecules, per second, will be

$$\frac{m}{r} (u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2)$$

The walls of the sphere will thus exert a force ( $F$ ) on the molecules which, according to Newton's Second Law, will be given by

$$F = \frac{m}{r} (u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2)$$

If  $p$  = the pressure exerted by the gas, then

$$p = \frac{F}{4\pi r^2} \text{ and}$$

if  $u$  = the root mean square velocity of the molecules\*

$n$  = the number of molecules present and

$v$  = the volume of the sphere (i.e. of the gas)

then since, by definition,

$$u^2 = u_1^2 + u_2^2 + u_3^2 \dots u_n^2$$

$$p = \frac{nm u^2}{v} \cdot \frac{1}{4\pi r^2} = \frac{nm u^2}{4\pi r^3}, \text{ and}$$

$$pv = \frac{nm u^2}{4\pi r^3} \cdot \frac{4}{3} \pi r^3 = \frac{1}{3} nm u^2$$

This may be written  $pv = \frac{2}{3} \cdot \frac{1}{2} nm u^2$ .

But  $\frac{1}{2} nm u^2$  is the total kinetic energy of the molecules, which will remain constant, provided that the temperature does not change. It follows, therefore, that at constant temperature,

$$pv = \text{Constant},$$

which agrees with *Boyle's Law*.

It has been shown (see page 27) that gases which exert no chemical or physical action on one another and which are under the same conditions of temperature and pressure can be mixed without change of temperature or pressure. Hence it is assumed that the molecules of equal volumes of two gases at the same temperature and pressure possess the same total kinetic energies.

From the equation above it is evident that the product  $pv$  is equal to two-thirds of the total kinetic energy of a gas. Hence, if the temperature be altered, pressure remaining constant, the kinetic energy (i.e., temperature) must alter to the same extent, and hence also the volume. Otherwise expressed, if the pressure remains constant, the same alteration of temperature will alter the volume to the same extent. This agrees with *Charles's Law*.

From what has been said we see that since equal volumes of two gases at the same temperature and pressure have the same value for the product  $pv$  that is

$$n_1 m_1 u_1^2 = n_2 m_2 u_2^2,$$

and further, since, as was shown by Clerk Maxwell, the average kinetic energy per molecule in the two systems will be the same when the temperature is the same, that is

$$\frac{1}{2} m_1 u_1^2 = \frac{1}{2} m_2 u_2^2,$$

it follows that

$$n_1 = n_2$$

which agrees with *Avogadro's hypothesis* (page 76).

It must be pointed out that this deduction of *Avogadro's hypothesis* depends upon the assumption that two gases are in thermal equilibrium when their kinetic energies are the same: which is an unverifiable assumption. This assumption can similarly be deduced from *Avogadro's hypothesis*. Hence the Kinetic Theory should not be quoted as *proof* of the truth of *Avogadro's hypothesis*.

Since  $pv = \frac{1}{3} nm u^2$ , the mean velocity

$$u = \sqrt{\frac{3pv}{mn}}$$

$$\text{Now the density of a gas } (d) = \frac{\text{mass}}{\text{volume}} = \frac{mn}{v}$$

\* Different molecules will, as mentioned previously, have different velocities.

The root mean square velocity is given by  $u = \frac{\sqrt{u_1^2 + u_2^2 + \dots + u_n^2}}{n}$  where

$u_1, u_2, \dots$  etc. are the velocities of individual molecules and  $n$  is the number of molecules present. If all the molecules were actually moving with this mean velocity the total kinetic energy would have the same value as the actual total kinetic energy.

Hence we have

$$u = \sqrt{\frac{3p}{d}}$$

or, in words, the mean velocity of a gas molecule is inversely proportional to the square root of its density. This is clearly in agreement with *Graham's Law of Diffusion*.

The Kinetic Theory not only correlates these previously discovered laws of the behaviour of gases, but also furnishes a means of calculating some molecular magnitudes.

Thus, since, as above, the mean velocity

$$u = \sqrt{\frac{3pv}{mn}}$$

For hydrogen at 0° C. and 760 mm. pressure we have

$$v = 1 \text{ c.c.}$$

$$p = 760 \text{ mm. of mercury} = 1,013,250 \text{ dynes per sq. cm}$$

$$mn = \text{mass of 1 c.c. of hydrogen at 0° C. and 760 mm} = 0.00008988$$

$$\text{hence } u = \sqrt{\frac{3 \times 1,013,250 \times 1}{0.00008988}}$$

$$= 184,000 \text{ cm. per sec. or 60 miles per min. nearly}$$

This result indicates that the mean velocity of the individual molecules is very much higher than the rate at which the gas diffuses as a whole. The reason for this is that the gas molecules can never move far in a straight line without colliding with each other: these collisions are so frequent (of the order of  $10^{28}$  per c.c. per second at S.T.P.) that the gas as a whole only moves forward at a relatively slow rate.

### § 13 Application of the Kinetic Theory of Liquids

It is a familiar fact of observation that gases and vapours (see page 46), if cooled sufficiently and subjected to sufficiently high pressures, condense into liquids, and it is evident from its nature that in a liquid the particles or molecules comprising the substance are definitely exerting a force of attraction upon each other, whatever may be true of gases in this regard (see page 42).

The discussion of the implications of the Gas Laws, and in particular of Charles's Law, has led (page 24) to a conception of an absolute scale of temperature, the absolute zero being taken to be  $-273^\circ \text{C}$ . The Kinetic Theory gives a further meaning to the absolute zero, since, in terms of that theory, it is that temperature at which all molecular motion ceases.

Conversely, molecular motion only ceases entirely, according to the Kinetic Theory, at the absolute zero, and it follows, therefore, that in ordinary liquids, molecular motion must still occur, although, owing to the existence of molecular attractions of considerable magnitude, its extent will be much restricted when compared with gases. In liquids there will be practically no free path (as is believed to exist in gases) and the motion of the molecules is thought to be more in the nature of a gliding of particles over and amongst each other.

A molecule in the body of a liquid will experience attraction on all sides equally, whereas one in the surface will experience a resultant



force directed towards the interior of the liquid owing to the absence of any marked attraction exerted on it from outside the liquid itself.

This is illustrated in Fig. 3.14 and shows that there will be in the surface of a liquid a force acting inwards towards the bulk of the liquid. The effects of this force are observed in the phenomenon of *surface tension* which thus becomes a logical consequence of the Kinetic Theory.

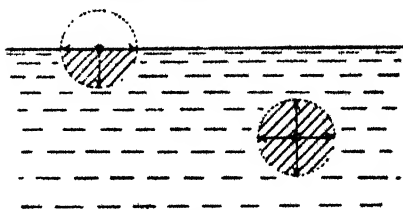


FIG. 3.14.—Molecular Forces in a Liquid

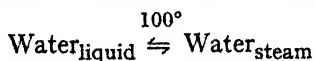
Although there can be practically no free path in liquids, nevertheless the speeds with which individual molecules are moving will, at any instant, vary considerably. Thus there will be a few molecules possessing kinetic energy greater than the average of the molecules as a whole, and if such a molecule should approach the surface it may have sufficient energy to travel clean through the surface into the space outside the liquid. This effect is observed in the phenomenon termed *evaporation*. The removal of such molecules from the liquid will result in a reduction in the mean kinetic energy of the liquid which thus will become cooler, or, if the temperature is to remain unchanged, heat must be supplied from the surroundings. This is the *latent heat* of evaporation.

The molecules of the substance which have escaped from the liquid in this way constitute a *vapour*\* in the space above the liquid. These molecules of vapour behave like those of an ordinary gas, and so they will be moving with high speeds. Some of these molecules will approach the surface of the liquid where some of them will be attracted by the molecules in the surface of the liquid and so be dragged into the liquid again. These molecules will be accelerated as they enter the liquid, owing to the forces acting upon them, and their capture will result in an increase in the mean kinetic energy of the liquid, whose temperature will rise in consequence. Heat is therefore given out on condensation.

Suppose now that a liquid is evaporating in a closed vacuous space. The fleetest molecules accumulate as a gas or vapour in the space above the liquid. The concentration of the vapour in the space above the liquid will go on increasing, but a certain percentage will plunge back into the liquid. The number of molecules which return to the liquid from the space above per second increases as the concentration of the vapour increases, although the rate at which the molecules leave the liquid probably decreases as the concentration of the vapour increases.

\* The distinction between "gas" and "vapour" is somewhat vague. If the "elastic fluid" be very far from its temperature of liquefaction, it is generally called a "gas"; and "vapour" if it is near its temperature of liquefaction. E.g., oxygen, nitrogen, etc., at ordinary temperatures are gases; whereas water or alcohol on evaporation would furnish vapours. Otherwise expressed, a gas is an elastic fluid at a temperature above its critical temperature, and a vapour is an elastic fluid below its critical temperature, but not in a liquid state.

When the number of molecules which return to the liquid in a given time is equal to the number of molecules which leave the liquid in the same time, the vapour is said to be saturated and the system in equilibrium. Thus,



This equilibrium, it will be observed, is not a static condition, that is, a state of rest; both processes are active (kinetic). There is a shower of molecules streaming into the liquid, and an efflux of molecules away from the liquid. The effect of one is neutralized by the other; neither can produce any visible result. Anything which disturbs this equality—e.g., a desiccating agent or a condenser in the space above (as in distillation), etc.—will alter the conditions.

If two glass tubes are taken, each about 80 cm. in length and sealed at one end, filled with dry mercury and inverted in dishes of mercury, the level of the mercury in each tube will sink somewhat but remain at such a height as represents the pressure of the atmosphere at the time of the experiment. The space above the mercury in such a tube is, to all intents and purposes, vacuum and is called a Torricellian vacuum (after Torricelli who, in 1643, first observed that mercury would only stand at a height of about 30 inches in such a tube). If a few drops of water are introduced by means of a small pipette into one of the tubes, the level of the mercury will be depressed further, and this process will continue on introduction of more water until a thin layer of water is seen resting on the surface of the mercury. The pressure exerted by the water vapour is equal to that of a column of mercury whose height is the difference between the heights of the mercury in the two tubes. The value of this pressure when the space is *saturated*, that is, when the addition of more water merely increases the amount of the liquid water layer visible on the mercury, without causing any increase in pressure, is called the *maximum vapour pressure*.

Experiments of this kind have shown that, at a given temperature, the maximum vapour pressure of a vapour in contact with its own liquid

is a constant quantity, and independent of the absolute amount of vapour and of liquid present in the system.

It is easy to see why this is so. If the surface of the liquid be doubled, it is true that twice as many molecules will leave the surface in a given time, but twice as many molecules will return.

If a barometer tube, such as was employed in the above experiments, be surrounded

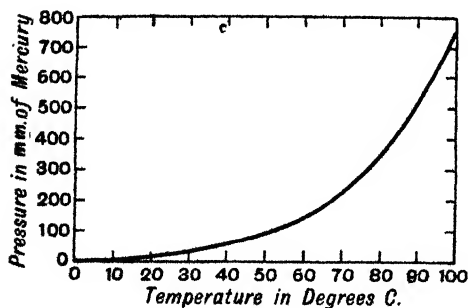


FIG. 3.15.—Vapour Pressure of Water

with a jacket through which warm water can be passed, and the maximum pressure of water (or other) vapour at various temperatures thus measured, we shall find that the higher the temperature, the greater the vapour pressure, provided all the liquid is not vaporized; but for any assigned temperature the maximum vapour pressure of a given liquid always has one fixed and definite value. (Cf. Fig. 3.15).

It has been shown that evaporation is (according to the Kinetic Theory) the result of the escape of the fastest-moving molecules in a liquid through the surface of the liquid. Consequently, anything which increases the number of swiftly moving molecules should assist the process of evaporation. Hence a current of air (through ether, for example) will remove these faster particles and lower the temperature in consequence. Supplying heat to the liquid so as to raise its temperature will also remove these fast-moving molecules, for we have seen that the mean speed of the molecules is increased by rise of temperature. When the temperature is high enough, the exposed surface of the liquid is not sufficient to allow the swift-moving molecules to escape fast enough; bubbles of vapour are accordingly formed *within* the liquid. Each bubble as it forms rises to the surface—increasing in size as it rises—and finally escapes into the atmosphere. The process of vaporization by bubble formation is called **boiling**; and the temperature at which boiling commences, the **boiling point** of the liquid. When the vapour pressure of the liquid is the same as the external pressure to which the liquid is subjected, the temperature does not rise any higher. Increasing the supply of heat only increases the rate at which the bubbles are formed so long as any liquid remains. Hence it is sometimes convenient to define: **The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the external pressure exerted at any point on the liquid surface.** This external pressure may be exerted by the atmospheric air, by vapour and air, by other gases, etc. Hence a table of the vapour pressures of a liquid at different temperatures also shows the boiling points of that liquid under different pressures. Thus water at a pressure of 4.6 mm. of mercury boils at 0° C. Hence liquids which decompose at their boiling point under ordinary atmospheric pressure can frequently be distilled without decomposition at the lower boiling temperature obtained by reducing the pressure. This is the basis of the process of **distillation under reduced pressure**, or, as it is sometimes less accurately styled, **distillation in vacuo**.

### § 14 Deviations from the Gas Laws—Van der Waals' Equation

We have seen how the simple gas equation,

$$pv = RT,$$

was arrived at; first, experimentally by the work of Boyle and Charles, and later, deduced theoretically by means of the Kinetic Theory. We have seen further that, while for many gases such as hydrogen, oxygen

c\*

546 PAR

and nitrogen at temperatures and pressures not far removed from atmospheric, this equation is substantially true, yet for many other gases (viz., those which can easily be liquefied), even under these conditions, serious deviations from the simple gas laws occur, and even the so-called permanent gases also exhibit deviations at very high pressures (compare pages 22, 27).

In deducing the gas laws from the Kinetic Theory, two simplifying assumptions were made (see page 36), viz.:

(i) that the molecules of a gas are of negligible size in comparison with the space they occupy, and

(ii) that the molecules do not exert any attraction on each other.

In a gas confined at high pressure these assumptions cease to be tenable, and account must be taken both of the actual size of the molecules of a gas and of the mutual attraction between them. One of the more important attempts to do this was due to Van der Waals, who reasoned somewhat as follows:

Let  $b$  denote the effective volume of a molecule as it moves to and fro between the boundary walls  $AB$ , Fig. 3.16. If this distance be halved to  $CD$ , Fig. 3.16,

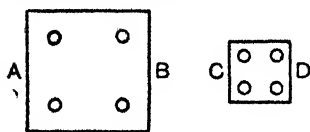


FIG 3.16

while the volume of the molecule remains constant, the molecule will have *less* than half its former distance to pass from one side to the other. It will therefore strike the walls more frequently than before. Hence the outward pressure of the molecule will increase more rapidly with decreasing volume than is described by Boyle's Law. Boyle's Law refers to the whole volume of the gas, but rather should

it refer to the space in which the molecules move. We therefore write  $v - b$  in place of  $v$  in Boyle's Law, and the result is

$$p(v - b) = RT$$

where  $b$  is called the "co-volume" or "vibratory volume" of the molecule.

It is evident that a force of attraction does exist between the molecules since condensation to a liquid occurs when the temperature of a gas or vapour is lowered, and it is clear that the closer the molecules are to one another, the greater will be the effect of the attractive forces between them. This attractive force will tend to make the gas occupy a smaller volume. The effect is much the same as if the gas were subjected to the action of a greater external pressure than the observed or apparent pressure of the gas.

It has been assumed that these attractive forces in the case of two portions of gas are proportional to the product of their masses. Since these are proportional to their densities, which are in turn inversely proportional to the volumes, we arrive at the conclusion that the attractive force is to be put as proportional to  $\frac{1}{v^2}$  or equal to  $\frac{a}{v^2}$  where  $a$  is a constant \*  $a/v^2$  must therefore be added to the observed pressure of the gas in order to indicate the total pressure tending to compress the gas. On correcting the equation  $p v = RT$  for the volume and the cohesion of the molecules, we obtain van der Waals' equation (1872):

$$\left(p + \frac{a}{v^2}\right) (v - b) = RT$$

\* Mellor has shown that this correction implies a force whose magnitude varies inversely as the fourth power of the distance; the force of gravity varies inversely as the square of the distance.

This amended equation agrees fairly well with a number of observations of gases under large pressures, and of gases which are near their points of liquefaction—e.g., ethylene, carbon dioxide, etc. It also describes many of the properties of liquids, and of the continuous passage of a gas to the liquid condition. The constants  $a$  and  $b$  must be evaluated from observations. The numerical values of the "constants" in van der Waals' equation are not always quite constant at different temperatures.

J. D. van der Waals (1888) found that for carbon dioxide,  $R = 0.00369$ ;  $b = 0.0023$ ; and  $a = 0.00874$ . This gas is known to deviate considerably from the behaviour required by Boyle's Law. On comparing the values of  $p\nu$  for carbon dioxide, calculated from the equation, at  $20^\circ$ :

$$\left(p + \frac{0.00874}{\nu^2}\right) (\nu - 0.0023) = 1.08$$

with the numbers observed by E. H. Amagat (1893) at  $20^\circ$ , we get:

$p$ atmospheres	$p\nu$	
	Observed	Calculated
1	1.000	1.000
50	0.680	0.678
75	0.180	0.170
100	0.228	0.226
200	0.419	0.411
500	0.938	0.936

The agreement between theory (van der Waals' equation) and fact (the observed data) is quite good. It will be remembered that if the gas behaves according to the equation  $p\nu = RT$ ,  $p\nu$  would have the same value for all pressures. As has been shown (page 22) the value of  $p\nu$  first decreases and then increases for all gases except hydrogen and helium. The two corrections act in opposite ways. At first the value of  $p\nu$  is decreased by the molecular attraction, and increased by the finite dimensions of the molecule. At low pressures, the correction for molecular attraction preponderates over that required for the volume of the molecule; while the correction for the volume of the molecules is relatively large when the volume of the gas is compressed very small by a large pressure. (Cf. pages 15, 18.) Several attempts have been made to improve the gas equation still further by the introduction of other terms, involving special constants which have to be evaluated from the experimental numbers, but they are of very limited application.

### § 15 The Critical Phenomena of Gases and Liquids

In 1869 T. Andrews found that if carbon dioxide at ordinary temperature be gradually compressed in a vessel suitable for the observation, the volume diminishes more rapidly than would occur if Boyle's Law correctly described the behaviour of the gas; and when the pressure attains a certain value, the gas begins to liquefy. A further decrease in the volume does not change the pressure, but only increases the quantity of gas liquefied. At length, when all the gas has liquefied, a large increase of pressure only causes a minute decrease in the volume of the liquid, since liquids in general undergo but a small change of volume on compression.

If the experiment be made with carbon dioxide at  $0^\circ$ , the gas commences to liquefy when the pressure has attained 35.4 atmospheres; if at  $13.1^\circ$ , liquefaction commences at 48.9 atmospheres pressure; if at  $30^\circ$ , at 70 atmospheres pressure; while if the temperature exceeds  $31^\circ$ , no pressure, however great, will liquefy the gas. Other gases exhibit similar phenomena. For each gas there is a particular temperature above which liquefaction is impossible, however great be the applied pressure. Andrews called this the **critical temperature** of the gas. The following are the critical temperatures of some common substances:

Hydrogen . . . . .	$-240^\circ$	Nitrous oxide . . . . .	$+36.5^\circ$
Nitrogen . . . . .	$-147^\circ$	Ammonia . . . . .	$+132^\circ$
Oxygen . . . . .	$-119^\circ$	Sulphur dioxide . . . . .	$+157^\circ$
Carbon dioxide . . . . .	$+31^\circ$	Water . . . . .	$+374^\circ$

The least pressure which is sufficient to liquefy the gas at the critical temperature is called the **critical pressure**; and the volume occupied by one gram-molecule of gas at the critical temperature and pressure

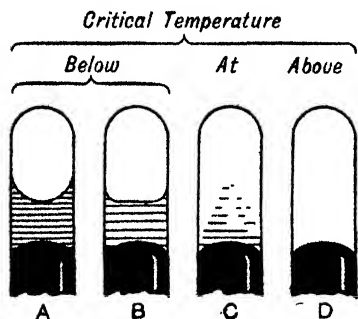


FIG. 3.17.—Diagrammatic Illustration of the Critical State of a Gas

is called the **critical volume**. It is interesting to notice the influence of temperature on carbon dioxide, partly liquid, partly gaseous. Fig. 3.17, *A*, represents the upper end of a glass tube in which the partly liquefied carbon dioxide is confined over mercury, at  $18^\circ$ . The surface of the liquid has a sharply defined curved meniscus. On raising the temperature, the meniscus of the liquid becomes flatter and flatter, Fig. 3.17, *B*, until, at  $31^\circ$ , Fig. 3.17, *C*, the surface seems to disappear. The sharp line of demarcation between the liquid and the gas vanishes. At  $40^\circ$ , the tube contains a homogeneous gas, Fig. 3.17, *D*. Liquid carbon dioxide cannot exist at this temperature, however great the pressure.

The relation between the pressure and the volume of, say, carbon dioxide, at different temperatures— $T$ ,  $T_c$ ,  $T_1$ ,  $T_2$ —is represented diagrammatically in Fig. 3.18. The portion of the curve  $K_2T_2$ , or  $K_1T_1$ , represents the behaviour of the gas when no liquid is present; the portion  $K_2M_2$ , or  $K_1M_1$ , the behaviour of the gas in the presence of its own liquid; and  $M_2P_2$  or  $M_1P_1$ , the behaviour of the liquid when no gas is present. It will be observed that  $K_2M_2$  and  $K_1M_1$  are straight lines parallel with the  $v$ -axis. This illustrates in a graphic manner the law previously considered: At any fixed temperature, the pressure of a gas in the presence of its own liquid is always the same. The curve  $T_cK_cP_c$  represents the relation between pressure and volume at the critical temperature; and the curve  $TP$  the relation between  $p$  and  $v$  at a temperature when the gas does not liquefy. The line  $K_cK_1K_2B$

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represents the condition under which the gas, compressed at the stated temperatures  $T_c$ ,  $T_1$ ,  $T_2$ , begins to liquefy, and it is hence called the **dew curve**, because a gas under a gradually increasing pressure first shows signs of liquefaction under conditions represented by a point on this line; similarly, the line  $K_cM_1M_2A$  is called the **boiling curve**,

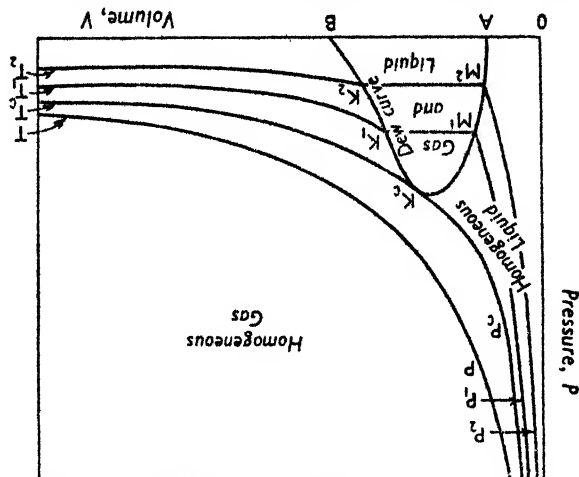


FIG. 3.18.— $p : v$ —Curves for Carbon Dioxide

because a liquid, under a gradually diminishing pressure, first shows signs of vaporization under conditions represented by a point on this line. Note also that the lines  $K_cA$ ,  $K_cB$  and  $K_cP_c$  divide the plane of the paper into three regions. Every point to the right of  $BK_cP_c$  represents a homogeneous gas; every point in the region  $AK_cB$  represents a heterogeneous mixture of gas and liquid; and every point to the left of  $AK_cP_c$ , a homogeneous liquid. The gas in the region  $K_cBVT_c$  is below its critical temperature, and is then said to be a vapour—*vide* page 39. The diagram, Fig. 3.18, thus represents the conditions of equilibrium of a liquid or a gas under different conditions of temperature, pressure or volume.

It is possible to calculate the value of the critical constants from van der Waals' equation, as follows.

Van der Waals' equation may be written as a cubic in  $V$ :

$$V^3 - \left(b + \frac{RT}{p}\right) V^2 + \frac{a}{p} V - \frac{ab}{p} = 0$$

This can have three roots. There may be only one real value of  $V$  which will satisfy the equation for a given temperature and pressure or there may be three such values. This latter case corresponds to curves such as  $P_2M_2K_2T_2$  (Fig. 3.18). At the critical point ( $K_c$ —Fig. 3.18) the three roots become identical and equal to the critical volume ( $V_c$ ). Hence at the critical point  $(V - V_c)^3 = 0$ . This equation

must be identical with van der Waals' equation when the temperature is equal to the critical temperature ( $T_c$ ) and the pressure is the critical pressure ( $p_c$ ).

$$\therefore V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 \equiv V^3 - \left(b + \frac{RT_c}{p_c}\right) V^2 + \frac{a}{p_c} V - \frac{ab}{p_c}$$

By equating coefficients of equal powers of  $V$  we have

$$3V_c = b + \frac{RT_c}{p_c}; \quad 3V_c^2 = \frac{a}{p_c}; \quad V_c^3 = \frac{ab}{p_c}$$

$$\text{Whence } V_c = 3b; \quad p_c = \frac{a}{27b^2}; \quad T_c = \frac{8a}{27Rb}$$

It is interesting to note historically that Cagnard de la Tour, in 1822, long before Andrews's experiment, noticed that when a liquid is heated in a sealed tube there is a definite temperature at which the surface of separation between the gas and liquid disappears, and the whole contents of the tube become homogeneous. Cagnard de la Tour's experiments thus demonstrate that the critical temperature is the upper limit to the liquid state; and Andrews's experiments prove that the critical temperature is the lower limit to the gaseous state. The passage from the one state to the other proceeds in a continuous manner. **The liquid and gaseous states are continuous, not abrupt.** The properties—density, surface tension, viscosity, refractive power, heat of vaporization, compressibility, etc.—of a liquid gradually lose their distinctive character as the temperature is raised, until, at the critical temperature, the properties of liquid and gas are the same.

## § 16 The Liquefaction of Gases

The familiar fact that a liquid such as water is converted by heat into a vapour (steam) and that the latter reverts to the liquid state on cooling makes it seem likely that many substances which ordinarily exist in the form of gases or vapours, such as ammonia or chlorine, would become liquid if cooled sufficiently. The difficulty of applying sufficient cooling, however, prevented an early verification of this surmise.

But the experiments of van Marum and of Northmore (1806), who succeeded in liquefying ammonia and chlorine respectively by the application of pressure, opened up a fruitful field of investigation.

In 1823 Faraday again succeeded in obtaining liquid chlorine, and in greater bulk than Northmore had done, by heating chlorine hydrate (page 534) in one limb of a tube shaped as in Fig. 3.19, while the other limb was cooled in a freezing mixture. By a suitable choice of materials he was able to

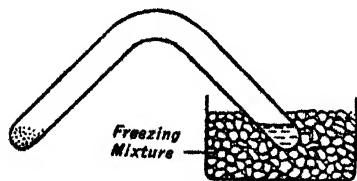


FIG. 3.19.—Faraday's Tube for liquefaction of Gases



liquefy hydrogen sulphide, hydrogen chloride, carbon dioxide, nitrous oxide, cyanogen, ammonia, and a number of other gases, but he failed to liquefy nitrogen, oxygen or hydrogen. These gases for many years resisted all efforts to reduce them to the liquid state. These attempts relied largely on the applications of very high pressures (thus Natterer used pressures up to 2790 atmospheres without success). In consequence of these failures, such gases as hydrogen, oxygen, nitrogen, methane and carbon monoxide were called *permanent gases*.

### § 17 The Liquefaction of the Permanent Gases

The clue to the difficulty experienced by the earlier workers when the liquefaction of the so-called permanent gases was attempted, was furnished by the work of Andrews who, as we have seen (page 43), investigated thoroughly the critical phenomena of gases. It thus became evident that the obstacle to success in the experiments previously performed was insufficient cooling.

This incited experimenters to concentrate their attention on methods for the production of lower temperatures than those previously obtainable, and a number of the "permanent" gases were liquefied in small quantities by Pictet, who used liquid carbon dioxide, boiling under reduced pressure, as a cooling medium, and by Cailletet, who allowed the highly compressed gas to expand suddenly so that in having to do a certain amount of work against the pressure, heat corresponding to this work was taken from the gas itself, whose temperature fell in consequence.

W. Cullen (1755) seems to have been the first to notice that the temperature of air is decreased by rarefaction, and increased by compression; and J. Dalton attempted to measure the effects. If a gas whose molecules exert no attraction on one another be confined in a suitable vessel, and compressed, the mechanical work employed in compressing the gas is equivalent to the product of the pressure and the change in volume. This energy is transformed into an equivalent amount of heat which raises the temperature of the gas. On the other hand, if the gas expands against atmospheric pressure, the gas will be cooled because the gas itself has done a certain amount of work equivalent to the product of the atmospheric pressure and the change in volume.

No heat is developed when an ideal gas expands into a vacuum because no external work is done by the gas. This was investigated experimentally by J. L. Gay-Lussac (1807) and by J. P. Joule (1845). Compressed air was allowed to expand into an evacuated vessel, and the result, as Joule expressed it, was as follows: "No change of temperature occurs when air is allowed to expand in such a way as not to develop mechanical power." Hence, it was also inferred that no work is performed under these conditions against intermolecular attractions.

Our study of Boyle's and Charles's Laws has taught us that intermolecular attractions occur with most gases. Hence, this latter deduction might be questioned. The experiments, however, were not sufficiently sensitive to detect the small change of temperature which does, in fact, occur when a gas expands *in vacuo*.

Later, in a more delicate experiment, J. P. Joule and W. Thomson (Lord Kelvin)—1852–62—forced a steady stream of gas slowly along a boxwood tube, in which was fixed a porous plug of absorbent cotton or silk. It was found that, at ordinary temperatures, the gas was cooler after passing through the plug than before reaching it. This is a direct experimental proof of the existence of intermolecular attractions.

In Joule and Thomson's experiments, the temperature of carbon dioxide, nitrogen, oxygen, and air fell about  $1^\circ$ , while the temperature of hydrogen gas rose about  $0.039^\circ$  above the initial temperature of the gas. If, however, the experiment be conducted at a lower temperature, hydrogen gas behaves like the other gases, and is cooled. **The change of temperature which occurs when a gas is driven through a small orifice is called the Joule-Thomson effect.** The theoretical fall of temperature when the pressure falls from  $p_2$  to  $p_1$  is about  $\frac{1}{2}^\circ$  per atm. difference, or more exactly, if  $T$  be the absolute temperature,

$$\text{Fall of temperature} = 75.35(p_2 - p_1)/T$$

If carbon dioxide at 4 atm. pressure at  $0^\circ$  in passing through a porous plug suffers a fall of pressure to one atm., the fall of temperature will be  $73.35 \times 3 \div 273$ , or  $0.828^\circ$ .

The Joule-Thomson effect was applied in 1894–5 to the liquefaction of air on a large scale by Linde in Germany, and by Hampson in England. By this method all gases except helium had been liquefied (many such as hydrogen and fluorine by Dewar) by the end of the nineteenth century, and many had also been solidified. Helium, which was found to have a critical temperature as low as  $-267.9^\circ$ , was finally liquefied by K. Onnes at Leyden in 1907 and solidified by Keesom in 1926, when a temperature of only  $0.89^\circ$  abs. was reached.

The production of liquid air is now a process of commercial importance. The principle of the Linde-Hampson method will be understood after an examination of Fig. 3.20. The air to be liquefied—freed from carbon dioxide, moisture, organic matter, etc.—enters the inner tube of concentric or annular pipes, *A*, under a pressure of about 200 atmospheres. This tube is hundreds of yards long and coiled spirally

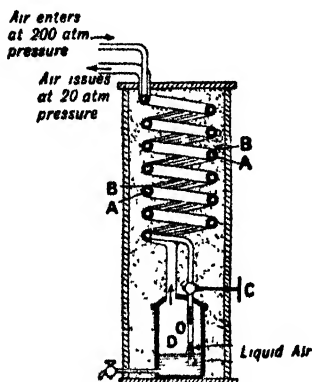


FIG. 3.20.—Linde's Apparatus for liquefying Air (diagrammatic)

to economize space. By regulating the valve *C* the compressed air suddenly expands in the chamber *D*. The air thus chilled passes back through the tube *B* which surrounds the tube *A* conveying the incoming air. The latter is thus cooled still more. The gas passes along to the pumps where it is returned with more air to the inner tube. In this manner, the incoming air at 200 atmospheres pressure is cooled more and more as it issues from the jet *O*. Finally, when the temperature is reduced low enough, drops of liquid air issue from the jet. The tubes must all be packed in a non-conducting medium to protect them from the external heat.

A further increase in the efficiency of the process has been secured by first cooling the air by means of liquid ammonia. Less power is required to liquefy ammonia than to compress and circulate the air so as to reduce its temperature to that of liquid ammonia.

It was suggested by Lord Rayleigh that the process could be made more efficient by allowing the expanding gas to do work in an expansion engine, whereby the heat equivalent to the work done by the engine is taken from the gas. This principle was applied by Claude in 1906 and is employed in modern liquid-air plant, the expansion engine being used to drive a dynamo, and thus a portion of the energy used in compressing the air is recovered, and at the same time the cooling is more rapid (page 50).

The temperature of liquid air is about  $-190^{\circ}\text{C}$ . and there is thus a far greater difference between its temperature and that of ordinary atmospheric air, than there is between the temperature of ice and boiling water. The preservation of liquid air is thus a far more difficult problem than would be involved in preventing cold water boiling away while surrounded by a steam jacket at  $200^{\circ}$ . James Dewar solved the problem by keeping the liquid air in a double (or triple) walled vessel with the space between the walls evacuated (Fig. 3.21). Glass is a poor conductor, and a vacuum is a non-conductor. Hence, the liquid in the inner vessel can receive heat only from above, and by radiation. The glass walls of the evacuated space are silvered to reduce the effects of radiant heat. Still air is a very bad conductor, so that the open end of the vessel is plugged lightly with cotton wool in order to reduce the ingress of heat from outside to a minimum. In this way, liquid air can be transported with surprisingly little loss.

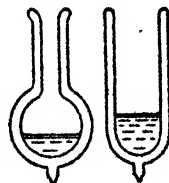


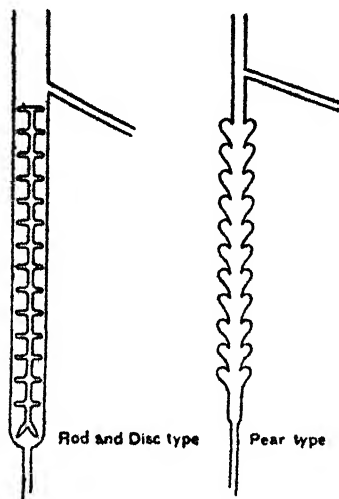
FIG. 3.21.  
Dewar Flasks

### § 18 The Manufacture of Oxygen and Nitrogen from Liquid Air

The boiling point of liquid nitrogen is  $-195.8^{\circ}\text{C}$ ., and that of liquid oxygen is  $-183^{\circ}\text{C}$ . There is thus a difference in boiling point of  $12.8^{\circ}\text{C}$ ., which, though small, is sufficient to allow of their separation by the evaporation of liquid air which is a mixture of the two.

Whenever a mixture of two liquids, of different boiling points, is made to evaporate the vapour which first comes off usually contains a greater proportion of the substance of lower boiling point, and the residual liquid will therefore be richer in the constituent of higher boiling point. Unless the liquids comprising the mixture are immiscible, or of very widely different boiling point, a complete separation is not possible by a simple distillation. Separation can be effected, however, by the use of a fractionating (or rectifying) column.

A fractionating column consists of a vertical tube so arranged that a portion of the vapour condenses in it and so runs back into the vessel in which the liquid is being heated. The construction of the interior of the column is such that the rising vapour is brought into thorough contact with the descending liquid (see Fig. 3.22). The rising vapour will contain the more volatile constituent (in larger quantity)



mixed with some of the less volatile one. The latter will condense more readily than the former so that a film of liquid will be found running down the tube, rich in the less volatile constituent. The rising vapour meeting this liquid heats it and so evaporates off from it a vapour relatively rich in the more volatile part, while condensing more of the less volatile portion in so doing. Thus, the rising vapour becomes steadily richer in the more volatile constituent as it passes up the tube, while the descending portion becomes richer in the higher boiling part. In this way an almost complete separation can be effected if an efficient column be used.

**FIG. 3.22.—Fractionating Columns** This principle is applied to the manufacture of oxygen and nitrogen from liquid air, oxygen being, as we have seen, the less volatile, and nitrogen the more volatile constituent.

The details of the process have varied since Linde (1895) first developed the method. In 1906 Claude introduced an improved apparatus involving two new principles. He made use of an expansion engine and he also liquefied the air in two stages so obtaining two liquids, one rich in oxygen and the other rich in nitrogen. In present-day plant this system of liquefaction is combined with fractionation in a Linde oxygen column (Fig. 3.23).

Air, freed from carbon dioxide, is compressed to a pressure of about 30 atm., becoming hot in the process. It is cooled to ordinary temperature by means of water and then still further cooled by the very cold gases (oxygen and nitrogen) escaping from the column through a heat exchanger. The cold compressed air is then made to do external work in the expansion engine by expansion to a pressure of about 4 atm.; as a consequence its temperature falls to about  $-170^{\circ}$  which is

not far above the liquefying point of air. This air is now fed into the lower part of the column (as shown in Fig. 3.23). The air then passes upwards through a series of plates (in part *A* of the column) down which an oxygen-rich liquid is trickling. Some evaporation from this liquid occurs making it progressively richer in oxygen as it descends and finally collects at *B* and it then contains about 50 per cent of each element. Much of the oxygen in the incoming air is condensed to a liquid at the same time. The remainder of this air, after rising through the plates, passes through a nest of vertical tubes, *D*, which are immersed in the pure liquid oxygen ultimately obtained. The air, still at 4 atm. pressure, liquefies partially at the temperature of boiling oxygen and the liquefied portion (containing about 40 per cent of oxygen) now, in turn, trickles down over the plates in part *A* of the column. The remaining air condenses finally in the tubes, *D*, and is almost pure nitrogen. It collects in an annular trough from which it is led to the top of the column while liquid air, rich in oxygen, is led from the bottom of the column and is reintroduced at a point about halfway between the top of

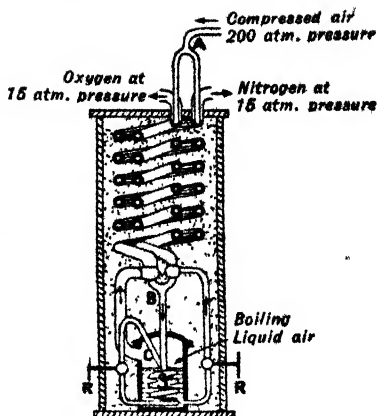


FIG 3 23

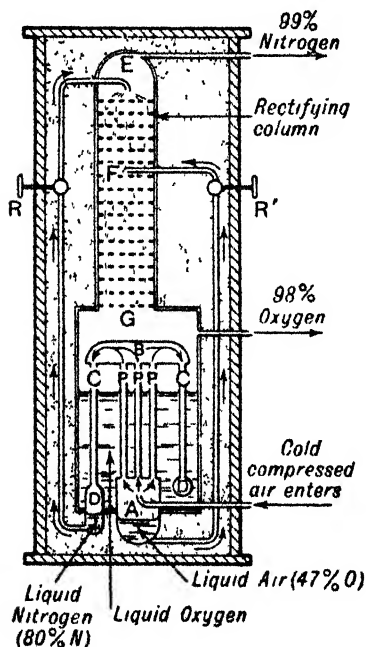


FIG. 3 24

the column and the nest of tubes. Pure nitrogen is thus evaporated from the liquid rich in nitrogen and passes out of the top of the column to the heat exchanger and pure oxygen collects as a liquid in *E*. Oxygen gas is led off by *F* also to the heat exchanger.

A diagrammatic sketch of Claude's apparatus is shown in Fig. 3.24. The cooled and purified air enters the lower part of the apparatus at a pressure of about 5 atm and rises through a series of vertical pipes *P* surrounded by liquid oxygen, where it is partially liquefied. The liquid containing about 47 per cent oxygen and 53 per cent of nitrogen drains into the lower vessel *A*. The vapour which has survived condensation enters *B* and then descends through a ring of pipes *C* arranged concentrically about the set previously described. Here all is liquefied. The liquid which ultimately collects in this vessel *D* is very rich in nitrogen. The pressure of the vapour in the central receptacle forces the liquid nitrogen to enter the summit of the rectifying column *E*, and the liquid, containing 47 per cent of oxygen, is likewise forced to enter the rectifying column at *F* lower down. The pressures and rates of flow are regulated by the cocks *RR'*. The liquid nitrogen is 3° or 4° lower in temperature than the liquid rich in

oxygen. Nitrogen evaporates from the down-streaming liquid, and oxygen condenses from the up-streaming gases. The heat supplied by the condensation of oxygen helps on the evaporation of nitrogen. Consequently, the descending liquid gets progressively richer and richer in oxygen, and the ascending gases richer in nitrogen. The liquid oxygen drains into the receptacle *G*, and is there evaporated by the latent heat of the gases condensing in the tubes. Finally, oxygen containing from 2 to 4 per cent of nitrogen passes from the oxygen exit, and nitrogen containing 0.2 to 1 per cent of oxygen escapes at the top of the rectifying column.

Most of the nitrogen and oxygen of commerce is now produced by processes such as these, whilst liquid air itself is a commercial product available in quantity.

## CHAPTER 4

# CHEMICAL CHANGE

The common operations of chemistry give rise in almost every instance to products which bear no resemblance to the materials employed. Nothing can be so false as to expect that the qualities of the elements shall be still discoverable in an unaltered form in the compound.—W. WHEWELL.

Nature in her inscrutable wisdom has set limits which she never oversteps.  
—JEAN REY.

### § 1 Physical and Chemical Changes

It is a commonplace of observation that changes are constantly taking place in all the substances which surround us; changes which may or may not have been induced by our own intervention. These changes are classified for convenience into two types, physical and chemical, and although, as is frequently the case with our attempts at classification, there is no sharp dividing line between the two, the conception underlying this classification is of fundamental importance in chemistry. Broadly speaking, it may be said that a *physical change* involves only a few of the properties of the substance undergoing it and is of such a kind as to give us no reason to suppose that a new substance has been formed; while on the other hand a *chemical change* is attended by so far-reaching and extensive an alteration of the properties of a substance that we are bound to conclude that a new substance has resulted.

In practice, three criteria are employed in distinguishing between physical and chemical changes. These are:

(i) Chemical changes are accompanied by a profound alteration in properties, while physical changes are partial in character;

(ii) Chemical changes are usually permanent, while physical changes continue only so long as the exciting cause remains and can take place and be repeated as often as this cause is in operation;

(iii) Chemical changes are usually attended with far greater energy changes than are physical.

When liquid water becomes ice or steam there is no change in the *chemical* nature of the substance, for the matter which makes steam and ice is the same in kind as that of liquid water. A substance can generally change its state, as when liquid water becomes steam or ice. The idea is further emphasized by the fact that in most cases a substance is called by the same name, whether it be in the solid, liquid, or gaseous state of aggregation, e.g., we speak of "liquid" oxygen, "liquid" air, "molten" silver chloride, etc. Again, matter may change its *volume* by expansion or contraction; it may change its *texture*, as when a porous solid is compressed to a compact mass; it

may change its *form*, as when matter in bulk is ground to powder; it may change its *magnetic qualities*, as when a piece of soft iron in contact with a magnet attracts other pieces of iron, etc. It is conventionally agreed to say that in none of these cases of physical change is there any evidence of the formation of a new substance; and that the matter does not lose or change those properties which distinguish it from other forms of matter.

When magnesium metal is heated in air, a white powder is formed, and when mercuric oxide is similarly treated, mercury and oxygen are obtained. The action of heat in both cases furnishes forms of matter with very different specific properties from those forms of matter employed at the start.

When water is heated it turns into steam, and when the source of heat is removed the steam condenses to water again. In contrast, when magnesium is heated in air the white powder resulting remains as such when the source of heat is removed, and shows no tendency whatever to revert to magnesium metal. The former of these is a physical, and the latter a chemical, change.

## § 2 Mixtures and Compounds

The investigation of samples of matter, whether as found naturally, or formed as the result of human intervention, soon reveals the fact that some samples are easily sorted into portions readily seen to be different, whereas others seem to be single substances. These last are sometimes called *pure substances*, and may be defined as single species of matter distinguished by exhibiting, under given conditions, characteristic and invariable properties. Samples of matter can thus be subdivided into mixtures and single (or pure) substances.

Pure substances may be of one of two kinds, viz., elements and compounds. From the time of Dalton until comparatively recently elements have been defined as substances which, so far, have not been resolved into any simpler form of matter. This definition is no longer completely satisfactory since the atom has been shown to possess a structure (Chapter 2). A more satisfactory definition is that elements are substances which have not been converted either by the action of heat, or chemical reaction with another substance or small electric potentials into any simpler electrically neutral form of matter. An element is also a pure substance which forms products of greater weight than itself in all chemical changes which it undergoes.

It is now necessary to consider the experimental tests necessary in order to distinguish a chemical compound from a mixture.

*Summary.*—The tests for distinguishing chemical compounds from mixtures involve answers to the following questions:

1. Are the different constituents united in definite and constant proportions?



2. Is the substance homogeneous?
3. Can the constituents be separated by mechanical processes?
4. Are the properties of the substance additive?
5. Were thermal, actinic, or electrical phenomena developed when the substance was compounded?

**1. The constituents of a compound are combined in definite proportions.**—If a substance produced in different ways be not constant in composition, it is not considered to be a chemical compound, but rather a mixture. R. Bunsen (1846), for example, showed that the proportion of oxygen to nitrogen in atmospheric air is not constant, because the oxygen varies from 20.97 to 20.84 per cent by volume, by methods of measurement with an error not exceeding 0.03 per cent. Hence, the oxygen and nitrogen in atmospheric air are said to be simply mixed together, and not combined chemically.

**2. Compounds are homogeneous, mixtures are usually heterogeneous.**—It is comparatively easy to detect particles of sugar and sand in a mixture of the two; and a simple inspection of a piece of Cornish granite will show that it is a mixture of three principal constituents—silvery flakes of mica, whitish crystals of felspar, and clear glassy crystals of quartz. Although the particles of felspar, mica and quartz differ from one another in size and shape, no essential difference can be detected in the composition and properties of different samples of pure quartz, pure felspar and mica. Hence, it is inferred that the sample of granite is a mixture of felspar, quartz and mica; and that each of these minerals is a true chemical compound. Very frequently, the constituents of a mixture are too small to be distinguished by simple inspection, and the body appears homogeneous. **A homogeneous substance is one in which every part of the substance has exactly the same composition and properties as every other part.** A microscopic examination may reveal the heterogeneous character of the substance. Blood and milk, for instance, appear to be homogeneous fluids, but under the microscope the former appears as a colourless fluid with the corpuscles in suspension; and milk appears as a transparent liquid containing innumerable globules (fat). Naturally, too, the stronger the magnification, the greater the probability of detecting whether the body is homogeneous or not. Sometimes the microscope fails to detect non-homogeneity under conditions where other tests indicate heterogeneity.\*

Before constant composition can be accepted as a proof of chemical combination, it must also be shown that the substance is homogeneous. A substance may have a fixed and constant composition and yet not be homogeneous—e.g., cryohydrates and eutectic mixtures to be described later (page 185). A substance may appear to be homogeneous and yet not have a constant composition—e.g., atmospheric air; a solution of sugar in water. This simply means that *all chemical*

\* See a later section on " Ultramicroscopic Particles " (page 283).

*compounds are homogeneous, but all homogeneous substances are not chemical compounds.* Indeed, it is sometimes quite impossible to tell by any single test whether a given substance is a mixture or a true chemical compound.

**3. The constituents of a mixture can usually be separated by mechanical processes.**—The properties of a mixture of finely powdered iron and sulphur have been used in chemical text-books since 1823 to illustrate the difference between mixtures and compounds. It would be difficult to find a better example. If a mixture containing, say, 6 grams of iron and 4 grams of roll sulphur be made in a mortar, it can be seen that: (1) the colour of the mixture is intermediate between the colour of the iron and of the sulphur; (2) the particles of iron and sulphur can be readily distinguished under the microscope; (3) some of the iron can be removed without difficulty by means of a magnet; and (4) the two can be separated quite readily by washing the mixture on a dry filter paper by means of carbon disulphide. The sulphur dissolves in the carbon disulphide; the solution can be collected in a dish placed below the filter paper; and the sulphur can be recovered by allowing the carbon disulphide to evaporate from the dish. Sulphur remains behind as a crystalline residue, while the metallic iron remains on the filter paper. Here then the constituents of the mixture have been separated by mechanical processes—the attraction of a magnet and the action of solvents. It is not always possible to apply these tests. Solvents, as we shall find later, sometimes decompose a compound into its constituents, or, conversely, “cause” the constituents of a mixture to combine.

**Mechanical processes of separation.**—The so-called mechanical processes of separation include: (1) Magnetizing, hand-picking, sieving, etc.; (2) Placing in liquids of the right specific gravity, when the lighter constituents will float, and the heavier constituents will sink; (3) Differing solubility of the constituents in suitable solvents; (4) Distillation; (5) Freezing; (6) Liquefaction; (7) Diffusion; (8) Elutriation; (9) Flotation.

It may be useful again to emphasize the fact that the so-called “mechanical” processes of separation, involving solution, freezing, and distillation, are not always satisfactory tests for distinguishing chemical compounds from mechanical mixtures. It is generally stated that “a solution of sugar or of salt in water is a mechanical mixture because, though homogeneous, the salt or sugar can be recovered unchanged from the water by the mechanical process of evaporation.” This is an unwarranted assumption. The salt and water might have combined, and the product of the chemical combination might have been decomposed into salt and water during the process of evaporation.

**4. A mixture usually possesses the common specific properties of its constituents; the properties of a compound are usually characteristic of itself alone.**—The properties of a mixture are nearly always additive, i.e., the resultant of the properties of the constituents of the mixture.

For instance, a mixture of equal parts of a white and black powder will be grey. The specific gravity of a mixture of equal volumes of two substances of specific gravity 3 and 5 will be 4, because if 1 c.c. of water weighs 1 gram, there will be a mixture of 0.5 c.c. weighing 1.5 grams of one substance; 0.5 c.c. of the other substance weighing 2.5 grams; and  $1.5 + 2.5 = 4$  grams per c.c.

If a portion of the mixture of sulphur and iron indicated above be placed in a hard glass test-tube, and warmed over the bunsen flame, the contents of the tube begin to glow and a kind of combustion spreads throughout the whole mass. If when cold the test-tube is broken, it will be found that (1) the porous dark mass formed during the action is quite different from the original mixture; (2) under the microscope the powdered mass is homogeneous; (3) it is not magnetic like iron (provided that the iron was not in excess); and (4) it gives up no sulphur when digested with carbon disulphide. These facts lead to the assumption that there has been a chemical reaction between the sulphur and the iron. *When chemical combination occurs, the reacting constituents appear to lose their individuality or identity more or less completely, and each new substance which is formed has its own distinctive properties.*

**5. Thermal, actinic (light), or electrical phenomena usually occur during chemical changes.**—Attention must be directed to the fact that a great deal of heat was developed during the combination of the iron and sulphur. The heat required to start the reaction does not account for the amount of heat developed during the reaction. This point is perhaps better emphasized by placing an intimate mixture of powdered sulphur and zinc on a stone slab. After the flame of a bunsen burner has been allowed to play on a portion of the mixture for a short time to start the reaction, the zinc and sulphur combine with almost explosive violence. Large amounts of heat and light are developed during the reaction.

If a plate of commercial zinc be placed in dilute sulphuric acid bubbles of gas are copiously evolved, and if a thermometer be placed in the vessel, the rise of temperature shows that heat is generated during the chemical action. If the zinc be pure, very little, if any, gas is liberated. It makes no difference if a plate of platinum be dipped in the same vessel as the zinc, provided the plates are not allowed to come into contact with one another. If the two plates are connected by a piece of copper wire, a rapid stream of gas bubbles arises from the surface of the platinum plate, and some gas also comes from the zinc plate. The platinum is not attacked by the acid in any way, but the zinc is rapidly dissolved. If a galvanometer or ammeter be interposed in the connection between the two plates the deflection of the needle shows that an electric current "passes" from the platinum to the zinc. The electric current is generated by the chemical reaction between the zinc and the acid, which results in the formation of zinc sulphate and a gas. The action will continue until either all the acid or all the zinc is used up.

*Nomenclature.*—The junction of the wire with the zinc plate is conventionally called the **negative** or **− pole**; and the junction of the wire with the platinum plate is called the **positive** or **+ pole**. The vessel of acid with its two plates is called a **voltaic cell**, and this particular combination can be symbolized:

Platinum | Dilute sulphuric acid | Zinc

The chemical reaction just indicated is far from being the most economical mode of generating electricity, but all the different forms of voltaic cell agree in this: **Electricity is generated during chemical action.**

*The development of heat, light, or electrification are common concomitants of chemical action.* The absence of such phenomena when substances are simply mixed together is usually taken as one sign that chemical action has not taken place. When nitrogen and oxygen are mixed together in suitable proportions to make atmospheric air there is no sign of chemical action, and this fact is sometimes cited among the proofs that air is a mixture. The argument is not conclusive, because the condensation of water vapour and the freezing of liquid water are often cited as examples of physical change although heat is evolved in both transformations.

The above list does not exhaust the available tests, but in spite of what we know, there is sometimes a lingering doubt whether a particular substance is a mixture or a true chemical compound. This arises from the fact that some of the tests are impracticable, others are indecisive. As previously stated, owing to our ignorance, it is not always easy to state "the truth and nothing but the truth."

Suppose a substance is suspected to be a chemical compound because it appears to be homogeneous; on investigation, we find that it has a fixed definite composition. This verifies our first suspicion, and the joint testimony gives a very much more probable conclusion than either alone. By piling up the evidence in this manner, for or against our suspicion, we can make a chain of circumstantial evidence which enables highly probable conclusions to be drawn. Each bit of evidence taken by itself is not of much value, but all the evidence taken collectively has tremendous weight. It is easy to see, too, that the probability that an hypothesis is valid becomes less as the number of unproved assumptions on which it is based becomes greater. On the other hand, plausible hypotheses neatly dovetailed may sometimes fit together so well as to strengthen rather than weaken one another; but the truth of the hypotheses is not thereby established.

We can even get a numerical illustration. If the definite-composition test be right nine times out of ten, the probability that a given substance of definite composition is not a true compound is  $\frac{1}{10}$ ; similarly, if the homogeneous test be right three times out of four, the probability that the given homogeneous substance is not a chemical compound is  $\frac{1}{4}$ ; and the probability that the given homogeneous substance of definite composition is not a true compound is  $\frac{1}{40}$ . **Every bit of additional evidence in favour of a conclusion multiplies the probability of**

its being correct in an emphatic manner; and evidence against a conclusion acts similarly in the converse way. Huxley has stated that one of the tragedies in science is the slaughter of a beautiful hypothesis by one *incongruent fact*; a conclusion based solely upon circumstantial evidence is always in danger of this Damoclean sword.

### § 3 The Law of Conservation of Mass

Lavoisier (1774) heated tin with air in a closed vessel and found that the weight of the whole system, before and after the calcination of the tin, was the same, thus showing that the whole system had neither gained nor lost in weight. This experiment demonstrated the fact that in spite of the most painstaking care, every time all the substances taking part in a chemical reaction are weighed before and after the change, there is no sign of any alteration in the quantity of matter. This fact is sometimes called the law of the indestructibility of matter and was tacitly assumed by many old investigators. A. L. Lavoisier is generally supposed to have first demonstrated the law in 1774 by experiments like that cited above, but the law was definitely enunciated in 1756 by M. W. Lomonosoff, and it must have been at the back of J. Black's mind when he worked on the alkaline earths in 1755.

The chemist's law of "the indestructibility of matter" really means that the total *weight* of the elements in any reacting system remains constant through all the physical and chemical changes it is made to undergo. The observed facts are better generalized as **the law of Conservation of Mass; no change in the total weight of all the substances taking part in any chemical process has ever been observed.** If  $A$  and  $B$  represent respectively the weights of two substances which take part in a chemical reaction, producing the weights  $M$  and  $N$  of two other substances, the law of conservation of mass states that  $A + B = M + N$  where "+" means "together with," and "=", produces. If the weight of one of these four substances be unknown, it can be computed by solving the equation. Chemists constantly use this principle in their work; for, as Lavoisier said: "Experiments can be rectified by calculations, and calculations by experiments. I have often taken advantage of this method in order to correct the first results of my experiments, and to direct me in repeating them with proper precautions."

When faith in magic was more prevalent than it is to-day, many believed that by some potent incantation or charm, matter could be called out of nothingness, or could be made non-existent.\* Superficial

\* H. Spencer considers that all the so-called experimental proofs by weighing tacitly assume the object being proved, since weighing implies that the matter forming the weights remains relatively unchanged in quantity; or, as H. S. Redgrove pointed out, weight measures matter because matter is indestructible, and matter is indestructible because weight measures matter.

observation might lead to the belief that a growing tree, the evaporation of water, and the burning of a candle prove the creation and the destruction of matter, but a careful study of these and innumerable other phenomena, has shown that the apparent destruction of matter

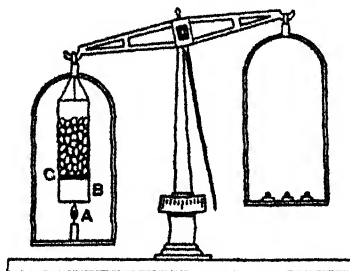


FIG. 4.1.—Apparent Increase in Weight during Combustion (after H. E. Roscoe and C. Schorlemmer)

is an illusion. Matter may change its state as when liquid water is vaporized, and when a candle is burnt. In the case of a growing tree, the nutrition the tree receives from the soil and from the air (carbon dioxide) is overlooked. Fig. 4.1 illustrates an instructive experiment which is commonly used to show that the apparent destruction of matter in the burning of a candle is illusory. A candle, *A*, is fixed on one pan of a balance below a cylinder

*B*. A piece of coarse wire gauze, *C*, is fixed in the lower part of the cylinder, *B*. The wire gauze supports a few lumps of quicklime\* on which rests a mixture of granulated soda lime and glass wool—the latter to prevent the soda lime clogging the tube. Weights are added to the right scale pan until the beam of the balance is horizontal. The candle is lighted. The gases rising from the flame pass through the cylinder *B*—and the products of combustion are absorbed by the soda lime. In three or four minutes the pan carrying the candle is depressed as illustrated in the diagram. The increase in weight is caused by the retention of the products of combustion by the soda lime. The products of combustion are formed by the combination of the carbon and hydrogen of the candle with the oxygen of the air. The oxygen of the air was not weighed in the first weighing.

Every time a chemical reaction takes place in a closed vessel, which permits neither the egress nor the ingress of matter, the total weight remains unchanged within the limits of experimental error. The more carefully the experiments are made, the more nearly do the values approach identity. Both A. Heydweiller (1901) and H. Landolt (1893) have tried to find if a loss in weight occurs during chemical action.

In 1900 the former reported the occurrence of small changes in weight when certain reactions were carried out in sealed vessels. Thus 80 gm. of copper sulphate dissolved in 150 c.c. of water and decomposed with 15 gm. of metallic iron appeared to suffer a loss in weight of 0.217 mgm.

Landolt conducted a series of experiments beginning in 1893 and continuing until 1908 in order to discover whether these losses were real or could be traced to some source, or sources, of error in the experiment.

\* To prevent water dropping on to the flame.

He placed in separate limbs of Jena glass tubes shaped as in Fig. 4.2, solutions of substances which react without the evolution of much heat (so that disturbances owing to this cause might be eliminated so far as possible) and sealed off the tubes. Examples of the substances he employed are:

- (i) silver nitrate and potassium chromate;
- (ii) slightly acidified potassium iodate and potassium iodide;
- (iii) lead acetate and sodium sulphide;
- (iv) acidified potassium chromate and sodium sulphite.

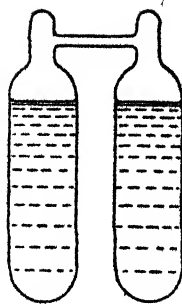


FIG. 4.2.  
Landolt's  
Experiment

The tubes were weighed, using exactly similar tubes as counterpoises, on a balance capable of detecting a change in weight of 1 part in 10,000,000 at its maximum load. One of the tubes was then tilted so as to cause reaction to take place and after cooling it was reweighed, when a very small change (usually a loss) in weight was noted. The counterpoise tube was then tilted and the processes repeated.

In the earlier experiments a slight change (maximum 0.167 mgm.) in weight was observed; but it was later found, after a very long series of experiments, that there were two causes for the change observed:

- (i) the slight evolution of heat caused the evaporation of traces of moisture condensed on the reaction vessel, and these traces did not recondense for a considerable time;
- (ii) the vessel suffered slight expansion owing to the heat evolution and did not recover its original volume until after the lapse of a long period.

By allowing the reaction vessels to stand for a long period after reaction had taken place before reweighing, Landolt found that they recovered their original weight within the limits of experimental error—in this case 1 part in 10,000,000. Landolt thus concluded that “since there seems no prospect of pushing the precision of the experiments further than the degree of exactness attained, the experimental proof of the law may be regarded as established.”

J. J. Manley in 1912, using a balance into which he had introduced many refinements, and applying corrections for, or taking precautions to avoid, certain possibilities of error in Landolt's experiments, was able to show that in the case of the reaction between barium chloride and sodium sulphate, any variation must be less than one part in 100,000,000.

It must be noted here that, according to the Theory of Relativity, matter and energy are interconvertible, being related according to the equation

$$E = mc^2$$

where  $E$  = energy liberated (or absorbed),  
 $m$  = loss (or gain) of mass,  
 and  $c$  = velocity of light.

In other words, instead of there being *two* fundamental principles expressed by the Law of Conservation of Mass *and* the Law of Conservation of Energy there is one principle only. In any chemical change, therefore, which is accompanied by a heat change there will be a corresponding change of mass. It is, consequently, no longer believed to be true that there is no change of mass in a chemical reaction but the value of  $c$  in the above equation is so large ( $3 \times 10^{10}$  cm. per sec.) that the loss of mass in any given laboratory experiment is extremely small. It is, in fact, of the order of  $10^{-11}$  gm. which is far outside the limits of experimental detection. The Law of Conservation of Mass is thus still a correct statement of the *experimental* facts.

#### § 4 The Law of Constant Composition

Attention must now be directed to the singular observation made by Jean Rey (1830) that during the calcination of a metal in air, "the weight of the metal increased from the beginning to the end, but when the metal is saturated, it can take up no more air. Do not continue the calcination in this hope: you would lose your labour." Experiments have shown that one gram, and only one gram, of air is absorbed by definite amounts of given metals under the conditions of the experiment, and Lavoisier's work (see page 59) proves that the *oxygen* of the air is alone absorbed. One part by weight of oxygen is found to be equivalent to:

Oxygen	Magnesium	Zinc	Aluminium	Copper	Tin
1	1.52	4.08	1.125	3.97	3.71

Instead of taking the weight of oxygen unity, it will be more convenient, later on, and also more in accord with general usage, to make oxygen 8 instead of unity. Hence, multiplying the preceding numbers by 8, we obtain:

Oxygen	Magnesium	Zinc	Aluminium	Copper	Tin
8	12.16	32.64	9	31.76	29.68

When magnesium is calcined in the presence of oxygen, the metal always unites with the oxygen in the proportion of one part of oxygen per 1.52 parts of magnesium, or 8 parts by weight of oxygen per 12.16 parts by weight of magnesium. The same principle obtains when magnesium oxide is made in several different ways; and likewise with the other metallic oxides. Hence, as P. G. Hartog puts it: **two like portions of matter have the same composition**. The converse of this statement is not necessarily true.

The exact work of J. S. Stas and of T. W. Richards and many others has firmly established this deduction for the regular type of chemical compounds. J. S. Stas (1860), for example, studied, among other things, the composition of silver chloride prepared by four different processes at different temperatures. He found that 100 parts of silver furnished 132.8425, 132.8475, 132.842, 132.848 parts of silver chloride;



and that neither the temperature nor the method of preparation had any influence on the composition of the chloride. The difference between the two extremes is less than 0.006 part per 100 parts of silver. This shows that the errors incidental to all experimental work are here remarkably small. Hence, Stas stated: "If the recognized constancy of stable chemical compounds needed further demonstration, I consider the almost absolute identity of my results has now completely proved it."

It must be noted that *the law of constant proportions cannot be proved with mathematical exactness. However skilful a chemist may be, it is impossible to make an exact measurement without committing an "error of observation" or an "error of experiment."* It is assumed that the small difference 0.005 per cent between the two extreme results of Stas (1) is wholly consequent upon the unavoidable errors of experiment, for we cannot expect an exact solution of the problem; and (2) is not the result of a very slight inexactitude in the law of constant proportions.

The composition of a definite chemical compound appears to be independent of its mode of formation, and therefore it is inferred that substances always combine in definite proportions. This deduction from the observed facts is called **the law of definite proportions**, or **the law of constant composition: a particular chemical compound always contains the same elements united together in the same proportions by weight**. This generalization was not discovered by any particular man, but gradually grew among the doctrines of chemistry. The law was tacitly accepted by many before it was overtly enunciated—e.g., by J. Rey (1630), I. Newton (1706), G. E. Stahl (1720), F. G. Rouelle (1764), C. F. Wenzel (1777), T. Bergman (1783), etc.

**The Proust-Berthollet Controversy.**—The validity of the law was the subject of an interesting controversy during the years between 1800 and 1808. J. L. Proust maintained that constant composition is the invariable rule; C. L. Berthollet maintained that constant composition is the exception, variable composition the rule. Proust's words are worth quoting:

According to my view, a compound is a privileged product to which nature has assigned a fixed composition. Nature never produces a compound, even through the agency of man, other than balance in hand, *pondere et mensura*. Between pole and pole compounds are identical in composition. Their appearance may vary owing to their manner of aggregation, but their properties never. No differences have yet been observed between the oxides of iron from the South, and those from the North; the cinnabar of Japan has the same composition as the cinnabar of Spain; silver chloride is identically the same whether obtained from Peru or from Siberia; in all the world there is but one sodium chloride; one saltpetre; one calcium sulphate; and one barium sulphate. Analysis confirms these facts at every step.

In more recent times the discovery of isotopes (pages 14 and 141) has indicated that the Law of Constant Composition is not absolutely true in all circumstances for all the atoms of a given element are not

necessarily identical in weight. For most of the ordinary operations of chemistry the Law holds since it is found that the proportions in which the isotopes occur in a given element are remarkably constant (with only a few exceptions) whatever the source of the element. In a few instances, notably that of lead (page 141), the atomic weight (that is, the weighted mean of the atomic weights of all the constituent isotopes) does show variation according to the source of the lead so that, for example, the Law of Constant Composition is not then exactly true, even within the limits of experimental error.

### § 5 The Law of Multiple Proportions

The formation of chemical compounds is not a capricious and fortuitous process, but it proceeds in an orderly fashion. Chemical combination is restricted to certain fixed proportions of matter. These limitations appear to have been prescribed by nature as part of her scheme in building the material universe. This fact arrested the attention of J. Rey in 1630. Rey's conclusion that in the calcination of the metals "nature has set limits which she does not overstep," agrees with many facts; but there are certain limitations. If one gram of lead be calcined for a long time at  $450^{\circ}$  to  $470^{\circ}$ , never more than 1.103 grams of a red powder—red lead—is obtained. Here, 64 grams of oxygen correspond with 621 grams of lead. If the lead be calcined at about  $750^{\circ}$ , one gram of lead will not take up more than 0.078 gram of oxygen to form a yellow powder—litharge; otherwise expressed, 64 grams of oxygen correspond with 828 grams of lead. Here then nature has set *two* limits; lead forms at least two definite oxides—a red oxide stable at a dull red heat, and a yellow oxide stable at a bright red heat. The relative proportions of lead and oxygen in the two oxides are as follows:

	Oxygen	Lead
Red oxide (red lead) . . .	64	$621 = 3 \times 207$
Yellow oxide (litharge) . . .	64	$828 = 4 \times 207$

This means that for a given weight of oxygen, the yellow oxide has four-thirds as much lead as the red oxide. Similarly, carbon forms two well-defined oxides called respectively carbon monoxide and carbon dioxide. In these we have:

	Oxygen	Carbon
Carbon dioxide . . . . .	8	$3 = 1 \times 3$
Carbon monoxide . . . . .	8	$6 = 2 \times 3$

At least five oxides of nitrogen are known. In these, the relative proportions of nitrogen and oxygen are as follows:

	Nitrogen	Oxygen
Nitrogen monoxide . . . . .	14	$8 = 1 \times 8$
Nitric oxide . . . . .	14	$16 = 2 \times 8$
Nitrogen trioxide . . . . .	14	$24 = 3 \times 8$
Nitrogen tetroxide . . . . .	14	$32 = 4 \times 8$
Nitrogen pentoxide . . . . .	14	$40 = 5 \times 8$

Starting from the compound with the least oxygen, for every 14 grams of nitrogen, the amount of oxygen increases by steps of 8 grams. Accordingly, in all five compounds of nitrogen and oxygen, the masses of nitrogen and oxygen are to one another as  $m \times 14 : n \times 8$ , where  $m$  and  $n$  are whole numbers. Several cases equally simple might be cited. Similar facts led J. Dalton (1802-4) to the generalization now called the **law of multiple proportions**: if two elements combine to form more than one compound the different weights of one which combine with the same weight of the other are in the ratio of simple whole numbers.

There is no difficulty in tracing the "simple ratio"  $m : n$  in the cases which precede, but it is not always easy to detect the *simplicity* of this ratio in perhaps the larger number of cases. For instance, the ratio  $m : n$  for compounds of carbon and hydrogen passes from 1 : 4 in methane, up to 60 : 122 in dimyricyl, and still more complex cases are not uncommon. Still the law is considered to be so well founded that it can be applied to predict the composition of compounds which have never been prepared. Thus, if an oxide of nitrogen containing rather more oxygen than nitrogen pentoxide be made, we may predict that it will contain  $6 \times 8 = 48$  parts of oxygen for every 14 parts of nitrogen by weight. Again, if a substance be found to contain oxygen and nitrogen, not in the proportion 14 : 8 or a multiple of 8, it is in all probability a mixture, not a true compound. Thus, air contains oxygen and nitrogen, but the proportion of nitrogen to oxygen is as 14 : 4.29. This is usually given along with other circumstantial evidence to show the probability that air is a mixture and not a chemical compound.

### § 6 The Law of Reciprocal Proportions

Between 1810 to 1812, J. J. Berzelius published the results of a careful study of the quantitative relations of some of the elements. He found that 100 parts of iron, 230 parts of copper, and 381 parts of lead are equivalent, for they unite with 29.6 parts of oxygen, forming oxides, and with 58.73 parts of sulphur, forming sulphides. Hence, since 58.73 parts of sulphur and 29.6 parts of oxygen unite respectively with 381 parts of lead, then, if sulphur and oxygen unite chemically, 58.73 parts of sulphur will unite with 29.6 parts of oxygen, or, taking the law of multiple proportions into consideration, with some simple multiple or submultiple of 29.6 parts of oxygen. In confirmation, Berzelius found that in sulphur dioxide, 58.73 parts of sulphur are united with 57.45 parts of oxygen. The difference between  $2 \times 29.6 = 59.2$  and 57.45 is rather great, but some of the methods of analysis were crude in the time of Berzelius, and very much closer approximations—very nearly 1 in 50,000—have been obtained in recent years.

J. B. Richter, some twenty years before Berzelius's work, proved that a similar relation held good for the reaction between acids and

alkalis. Berzelius extended Richter's Law\* to combinations between the elements. The above relations are included in the generalization sometimes called the **Law of Reciprocal Proportions**. **The proportions by weight in which two elements respectively combine with a third element are in a simple ratio to the proportions by weight in which the two elements combine with one another.** If two substances, *A* and *B*, each combine with a third substance *C*, then *A* and *B* can combine with each other only in those proportions in which they combine with *C*, or in some simple multiple of those proportions.

If a compound be formed by the union of two elements *A* and *B*, it is only necessary to find the proportion in which a third element *C* unites with one of the two elements, say *A*, to determine the proportions in which *C* unites with *B*. These numerical relations come out very clearly by comparing the proportions in which the different members of a series of elements, selected at random, combine with a constant weight of several other elements. Suppose the analysis of a substance shows that its ingredients are not in those proportions which we should expect from the known combinations of each of its components with another substance, we might safely infer that the substance analysed is a mixture, and not a single compound.

### § 7 Combining Weights, or Equivalent Weights

The following numbers represent the results obtained by the chemical analysis of a number of substances selected at random:

	Per cent		Per cent
Silicon dioxide . . . .	Silicon 46.75;	Oxygen 53.25	
Hydrogen chloride . . . .	Hydrogen 2.76;	Chlorine 97.23	
Magnesium chloride . . . .	Magnesium 25.53;	Chlorine 74.47	
Water . . . . .	Hydrogen 11.18;	Oxygen 88.81	
Silver chloride . . . . .	Silver 75.26;	Chlorine 24.74	
Silver fluoride . . . . .	Silver 85.025;	Fluorine 14.975	

Taking one of the elements as a standard, e.g., oxygen = 8, the amount of each of the other elements which will combine with this standard quantity of the selected element can be calculated. Starting with silicon, 53.25 parts of oxygen are combined with 46.75 parts of silicon, or 7.02 parts of silicon to 8 parts of oxygen. Similarly, for water, hydrogen is 1.008 when oxygen is 8. Again, in hydrogen chloride, when hydrogen is 1.008, chlorine is 35.46; in silver chloride, silver is 107.88 when chlorine is 35.46; when silver is 107.88, fluorine is 19; and when chlorine is 35.46, magnesium is 12.16. Collecting together the results:

Oxygen	Silicon	Hydrogen	Chlorine	Silver	Fluorine	Magnesium
8	7.02	1.008	35.46	107.88	19	12.16

\* C. F. Wenzel, 1777, is sometimes said to be the father of this generalization. This, however, appears to be an historical error.

On page 62 a number of results were obtained for some metals for the standard  $O = 8$  by a different process, and the number for magnesium obtained by an indirect process: Oxygen  $\rightarrow$  hydrogen (water)  $\rightarrow$  chlorine (hydrogen chloride)  $\rightarrow$  magnesium (magnesium chloride) gives the same result within the limits of experimental error as was obtained by a totally different process. Similar results are obtained in all cases, subject, of course, to the greater risk of experimental error when a long chain of compounds is involved.

These numbers are known as the combining weights, or equivalent weights of the respective elements, for from them it is possible to deduce the important generalization that **a number can be assigned to each element which represents the number of parts by weight of the given element which can enter into combination with 8 parts by weight of oxygen.** All combining weights are relative numbers, and they are conventionally referred to oxygen  $= 8$ .

The quantity of 8 parts by weight of oxygen has been adopted as the standard for equivalent weights since oxygen forms a compound with all the elements except the inert gases, and the adoption of this standard gives a series of numbers, none of which is less than one, and most of which are very close to whole numbers.

We thus arrive at the following definition:

**The combining weight or chemical equivalent of an element is the number of parts by weight of it which combine with, or replace, 8 parts by weight of oxygen, or the combining weight of any other element.**

### § 8 The Atomic Theory

The four laws of chemical combination: (1) the Conservation of Mass; (2) the law of Constant Composition; (3) the law of Multiple Proportions; and (4) the law of Reciprocal Proportions, summarize observed facts. They exist quite independently of any hypothesis we might devise about their inner meaning; but we have an intuitive feeling that there must be some peculiarity in the constitution of matter which will account for these facts.

**Dalton's atomic hypothesis.**—It is impossible to say who invented the atomic theory, because it has grown up with chemistry itself. For long the hypothesis was little more than an inanimate doctrine. It remained for Dalton to quicken the dead dogma into a living hypothesis. As explained in Chapter 2 (page 12) John Dalton (1801) employed the atomic hypothesis to explain the diffusion of gases, and later (1803) the structure of matter and of chemical combinations. A very brief statement of the so-called Dalton's atomic theory has been given already in Chapter 2, but may be repeated here for the sake of completeness:

1. Atoms are real discrete particles of matter which cannot be subdivided by any known chemical process.
2. Atoms of the same element are identical, especially in weight.

3. Atoms of different elements differ from each other and have different weights.

4. Compounds are formed by the union of atoms of different elements in simple numerical proportions.

5. The combining weights of the elements represent the combining weights of their atoms.

The hypothesis of Dalton respecting atoms, and more particularly atomic weights, is not quite that which prevails in modern chemistry. John Dalton considered the atom to be indivisible, and this is expressed in his aphorism: "Thou knowest no man can split an atom." T. Graham defined the atom not as a thing which cannot be divided but as one which had not been divided. The modern idea is that while the atom is perdurable in chemical changes it can be resolved into component parts. (Cf. Chapter 10.)

### § 9 The Atomic Theory and the Fundamental Laws of Chemistry

It is necessary now to consider how far the Atomic Theory, as propounded by Dalton, agrees with the facts. The most important evidence for it which was available in Dalton's time was its explanation of the fundamental laws of chemistry, viz., the Laws of Constant Composition, of Multiple Proportions and of Reciprocal Proportions.

Since, according to the theory, the atoms are chemically indivisible and indestructible, chemical changes must consist of a rearrangement or interchange of these atoms. No change in weight is to be anticipated from a mere redistribution of portions of matter, the total amount of which remains constant. Hence the atomic theory is in accord with the Law of Conservation of Mass.

When two elements unite to form a compound they do so, according to the theory, because atoms of each element unite in simple numerical proportions, and in any one particular compound this proportion is fixed. Hence, if all the atoms of one element are alike (particularly in weight),\* the proportions by weight in which the two elements combine to form a given compound must always be the same. This is the Law of Constant Composition.

Suppose that two elements *A* and *B* can give rise to three different compounds and suppose that in these there are *c* atoms of *A* united with *d* atoms of *B* in the first, *n* of *A* and *m* of *B* in the second, and *x* of *A* with *y* of *B* in the third. Then the composition by weight of each compound will be:

$$(i) \quad ca : db$$

$$(ii) \quad na : mb$$

$$(iii) \quad xa : yb$$

where *a* is the weight of an atom of *A* and *b* that of an atom of *B*.

\* Now known to be not exactly correct (see pages 14 and 141).

Writing these slightly differently, we have:

$$(i) \quad a : \frac{d}{c} b$$

$$(ii) \quad a : \frac{m}{n} b$$

$$(iii) \quad a : \frac{x}{y} b$$

The weights of element  $B$  combined with a fixed weight of element  $A$  will thus be in the proportion:

$$\frac{d}{c} : \frac{m}{n} : \frac{x}{y}$$

or clearing of fractions:

$$dnx : mcx : ycn.$$

Now all these several quantities are small whole numbers, by the theory, hence each of the products  $dnx$ ,  $mcx$ ,  $ycn$  will likewise be an integer. That is, the proportions of  $B$  combining with a fixed weight of  $A$  in each of the three compounds is a small whole number. This is the Law of Multiple Proportions.

An exactly similar process of reasoning from the postulates of Dalton's Theory shows it to be in accord also with the Law of Reciprocal Proportions.

### § 10 The Atomic Theory and Atomic Weights

Dalton's Atomic Theory is thus able to give a basis for the fundamental laws of chemistry as deduced by experiment; but there is one direction in which it proved to be incomplete.

According to the atomic theory, **an atom is the smallest particle of an element which can enter into or be expelled from chemical combinations.\*** How is the "smallest combining weight" of an atom to be fixed? In carbon monoxide, for example, we have oxygen and carbon in the following proportions by weight:

$$\text{Oxygen : Carbon} = 8 : 6$$

and in carbon dioxide

$$\text{Oxygen : Carbon} = 8 : 3.$$

What is the atomic weight of carbon if the atomic weight of oxygen is 8? Obviously the evidence now before us would be consistent with

\* If we think of the derivation of the word *atom*—from the Greek *ἀτομος* (*temno*), I cut—"that which cannot be subdivided," we must now add "chemically." But this definition of the atom says nothing about subdivision; nor about the ultimate nature of the atom. The term "atom" was once used to represent the "smallest interval of time," a "moment."

many different views. Carbon monoxide may be a compound of one oxygen atom with two carbon atoms, each with a combining weight of 3; or a compound of one oxygen atom with one carbon atom with a combining weight of 6. In the latter case, carbon dioxide is a compound of one carbon atom combining weight 6 with two oxygen atoms, and the same combining weights would have been obtained if any number  $n$  of carbon atoms were combined with  $2n$  oxygen atoms. Similar difficulties arise when we apply the idea of atoms so far developed to other combinations of the elements. There is, therefore, some confusion. The concept of the atom is insufficient for the development of a consistent system solely on the basis of the atomic hypothesis as propounded by Dalton. **Dalton's theory alone is thus not enough to fix the atomic weights of the different elements.**

The way out of the difficulty was ultimately found as a result of the work of Avogadro, and this must form the subject-matter of the next chapter.

### § 11 Chemical Symbols and Nomenclature

**Naming the elements.**—A great number of the elements have been christened with names derived from Greek roots. E.g., *iodine*—from its violet vapour; *chlorine*—from its green colour; *chromium*—from the colour of its compounds; *rhodium*—from the rose colour of its salts; *osmium*—from the pungent smell of osmic acid; *helium*—from its occurrence in the sun; *argon*—from its indifference to chemical reagents, etc. Other elements have been named more or less capriciously: thus some elements are named after particular localities—*strontium*, from Strontian (in Scotland); *ruthenium*, from Ruthenia (Russia); *yttrium*, *ytterbium*, *erbium* and *terbium* are all derived from Ytterby (in Sweden); *palladium* is a name given in honour of the discovery of the planetoid Pallas; *uranium* in honour of the discovery of the planet Uranus; *beryllium* is derived from the name of the mineral beryl; *zirconium*, from the mineral zircon; *platinum*, from the Spanish “plata,” silver; *thorium*, from “Thor,” the son of Odin, a god in Scandinavian mythology; *vanadium*, from a Scandinavian goddess, Vanadis; *tantalum*, from Tantalus in Grecian mythology; and *niobium*, from Niobe, daughter of Tantalus.

**Symbols.**—The old alchemists used to represent different substances by symbols. For example, gold was represented by the symbol ☉ or ★, for the sun; silver, by ☾, the moon. Lavoisier used the symbol ∇ for water; ♂ for oxygen. Dalton made a step in advance by representing the atoms of the elements by symbols, and combining these symbols so as to show the elements present in a compound. Thus, ☉ represented hydrogen; ○ oxygen; ● carbon. Water was represented by ☉○; carbon monoxide by ○●; carbon dioxide by ○●○. These symbols have all been abandoned. They are too cumbersome. To-day we follow J. J. Berzelius's method, suggested in 1811, and use one or two letters from the recognized name of the



element to represent any particular element. Thus, O represents an atom of oxygen; H, an atom of hydrogen; C, an atom of carbon; N, an atom of nitrogen, etc. The names of eleven elements start with C, and to prevent the possibility of confusion, a second leading letter is selected either from the name, or from the alternative Latin name of the element. Thus, C (carbon), Ca (calcium), Cd (cadmium), Ce (cerium), Cf (californium), Cl (chlorine), Cm (curium), Co (cobalt), Cr (chromium), Cs (caesium), and Cu (cuprum, copper). The elements with alternative Latin names are symbolized: Sb for antimony (Lat. stibium); Cu for copper (Lat. cuprum); Au for gold (Lat. aurum); Fe for iron (Lat. ferrum); Pb for lead (Lat. plumbum); Hg for mercury (Lat. hydrargyrum); K for potassium (Lat. kalium); Na for sodium (Lat. natrium); and Sn for tin (Lat. stannum).

**The evolution of chemical nomenclature.**—Until nearly the end of the eighteenth century, no systematic attempt had been made to name chemical substances in such a way as to indicate their composition. The names then in vogue were more or less arbitrary, for they were relics of alchemical terms—e.g., *crocus martis*—or derived from their discoverer—e.g., *Glauber's salt*—or based on some superficial resemblance furnishing what J. B. Dumas called the language of the kitchen. Thus antimony trichloride was called *butter of antimony*; zinc chloride, *butter of zinc*; and arsenic chloride, *butter of arsenic*. Similarly with oil of vitriol, olive oil, etc.; spirits of wine, spirits of salt, etc. T. Bergman and G. de Morveau simultaneously and independently attempted to devise a more complete system of naming chemical compounds. A. L. Lavoisier presented a report to the French Academy and terms like "ic" and "ate," and "ous" and "ite" were employed. J. J. Berzelius followed up the subject, and inaugurated the system which is virtually that employed to-day.

**Naming the compounds.**—Each element forms with other elements a group of compounds which are said to *contain* the respective elements, because the elements in question can be obtained unchanged from the compounds. Consequently **every compound has an elementary or ultimate composition**. Compounds are symbolized by joining together the letters corresponding with the different elements in the compound. Thus HgO represents a molecule of mercury oxide, a compound of mercury and oxygen. When only two elements are united to form a compound, the name of the second element is modified so that it ends in **-ide**.

The symbol for the element also represents one of its atoms. If more than one atom is present in a compound, a small figure is appended to the bottom\* right-hand corner of the symbol for an atom of the element, to indicate the number of atoms present. Thus H<sub>2</sub>O represents a molecule of water, i.e., a compound containing two atoms of hydrogen and one of oxygen; CO represents a molecule of carbon monoxide—a compound containing one atom of carbon and one

\* In France, generally at the top.

atom of oxygen;  $\text{Na}_2\text{CO}_3$  represents a molecule of sodium carbonate—a compound containing two atoms of sodium, one atom of carbon, and three atoms of oxygen. A number affixed in front of a group of symbols represents the number of times that group occurs in the given compound. Thus crystallized sodium carbonate is symbolized  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . This means that this compound contains the equivalent of one  $\text{Na}_2\text{CO}_3$ , and ten equivalents of the group  $\text{H}_2\text{O}$ .

Compounds of one element with oxygen are called **oxides**, and the process of combination is called **oxidation**. When an element forms more than one oxide, a Greek numerical suffix is often prefixed to the word "**oxide**." Thus,  $\text{SO}_2$  is sulphur dioxide;  $\text{SO}_3$ , sulphur trioxide;  $\text{CO}$ , carbon monoxide;  $\text{CO}_2$ , carbon dioxide;  $\text{PbO}$ , lead monoxide;  $\text{PbO}_2$ , lead dioxide.

Sometimes the termination **-ic** is affixed to the name of the metal for that oxide which contains the greater proportion of oxygen, and **-ous** for the oxide containing the lesser proportion of oxygen.\* For instance,  $\text{SnO}$  is either stannous oxide or tin monoxide;  $\text{FeO}$  is ferrous oxide; and  $\text{Fe}_2\text{O}_3$  ferric oxide. The last-named method of naming the compounds is not always satisfactory when the elements form more than two compounds. To get over the difficulty, a prefix **hypo-** (meaning "under," or "lesser") is sometimes added to the compound containing the least, and **per-** ("beyond," "above") is added to the one with the most oxygen. Thus:

Persulphuric acid	. . . $\text{H}_2\text{S}_2\text{O}_8$	Perchloric acid	. . . $\text{HClO}_4$
Sulphuric acid	. . . $\text{H}_2\text{SO}_4$	Chloric acid	. . . $\text{HClO}_3$
Sulphurous acid	. . . $\text{H}_2\text{SO}_3$	Chlorous acid	. . . $\text{HClO}_2$
Hyposulphurous acid	. . . $\text{H}_2\text{S}_2\text{O}_4$	Hypochlorous acid	. . . $\text{HClO}$

Oxides like alumina— $\text{Al}_2\text{O}_3$ ; ferric oxide— $\text{Fe}_2\text{O}_3$ , etc., are sometimes called *sesquioxides* (Latin, *sesqui*, one-half more).†

The nomenclature of inorganic chemistry is thus based upon the principle that the different compounds of an element with other elements can be named by a simple change in the beginning or termination of the word—witness ferric and ferrous oxides; and also by the addition of a numerical suffix showing the relative number of atoms of the corresponding element in its compounds.

\* For historical reasons, the names of some compounds do not conform to this system because the affix "**ic**" was assigned to the compound first discovered, and the compounds subsequently discovered were named accordingly.

† The oxides can be roughly divided into two classes. Some oxides, with water, form acids, and others act as bases. It is not very easy, at this stage of our work, to draw a sharp line of demarcation between the two. The *acidic oxides* have a sour taste, and turn a solution of blue litmus red; the *basic oxides* turn a solution of red litmus blue, and have a soapy feel.

## CHAPTER 5

### AVOGADRO'S HYPOTHESIS AND MOLECULES

Avogadro's hypothesis affords a bridge by which we can pass from large volumes of gases, which we can handle, to the minuter molecules, which individually are invisible and intangible.—W. A. SHENSTONE.

Thou hast ordered all things in measure, and number, and weight.—WISDOM OF SOLOMON.

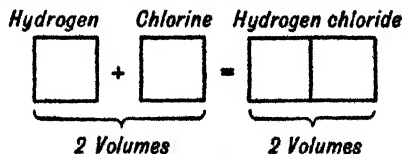
#### § 1 Gay-Lussac's Law of Combining Volumes

NOT very long after Dalton had directed the attention of chemists to the relations existing between the weights of elements which combine in different proportions, Gay-Lussac established a similar correspondence between the volumes of combining gases. A. von Humboldt, the naturalist and explorer, collected samples of air from different parts of the world, and, with the aid of J. F. Gay-Lussac, analysed the different samples with the idea of finding if the composition of air was variable or constant. Gay-Lussac used Cavendish's process—explosion of a mixture of air and hydrogen gas. As a preliminary, Humboldt and Gay-Lussac investigated the proportion by volume in which hydrogen and oxygen combine, and found the ratio of hydrogen to oxygen, by volume, to be nearly as 2 : 1, provided that the measurements are made under comparable conditions of temperature and pressure. If either hydrogen or oxygen were in excess of these proportions, the excess remained, after the explosion, as a residual gas. Humboldt and Gay-Lussac (1805) found:

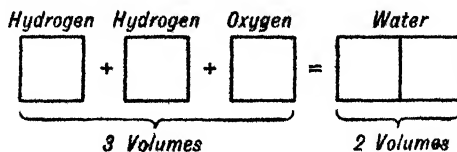
Vols. oxygen	Vols. hydrogen	Vols. residue
100	300	101.1 hydrogen
200	200	101.7 oxygen

After making corrections for impurities, etc., in the gases, Gay-Lussac and Humboldt stated that "100 volumes of oxygen required for complete saturation 199.89 volumes of hydrogen, for which 200 may be put without error."

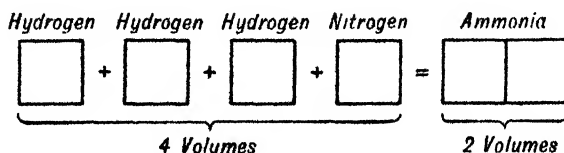
Struck by the simplicity of the relation thus found, J. F. Gay-Lussac (1808) followed up the subject by numerous experiments with different gases. As a result, he concluded that "gases always combine in the simplest proportions by volume." For instance, under the same conditions of temperature and pressure, one volume of hydrogen combines with one volume of chlorine forming two volumes of hydrogen chloride; this fact can be represented diagrammatically:



Two volumes of hydrogen combine with one volume of oxygen forming two volumes of water vapour (which condenses to liquid water if the temperature be below  $100^{\circ}$ ).



Three volumes of hydrogen and one volume of nitrogen form two volumes of ammonia. Thus:



Accordingly, we define **Gay-Lussac's Law**: when gases react together, they do so in volumes which bear a simple ratio to one another, and to the volume of the gaseous product of the action, provided that all measurements are made under the same conditions of temperature and pressure.

More recent investigations of the combining volumes of gases, carried out with many refinements in order to ensure a high degree of accuracy, have shown that the law is not exact. Thus A. Scott in 1893, using pure hydrogen prepared by passing steam over sodium, and oxygen obtained from silver oxide, and replacing the grease normally used for the lubrication of stopcocks by syrupy phosphoric acid (in order to eliminate the error which he found to be caused by the carrying over of this grease into the explosion vessel), found that hydrogen and oxygen combine at S.T.P. in the ratio 2.00285 : 1.

More recently Burt and Edgar, in 1915, as a result of 59 determinations, concluded that the ratio is 2.00288, thus agreeing with Scott's value very closely. The special features of their work were: (i) the use of very pure gases, prepared by special methods and subjected to rigorous purification and examination before use; (ii) the making of all measurements actually at  $0^{\circ}$  C. and 760 mm. pressure in order to avoid all uncertainty due to deviation of the gases from Boyle's and Charles's Laws.

The gases were obtained by the electrolysis of barium hydroxide solution. The hydrogen was passed over caustic potash and phosphorus pentoxide to dry it, and further purified either by the action of coconut charcoal at the temperature of liquid air, which readily absorbs nitrogen and oxygen, but which scarcely affects hydrogen, or by passing it over palladium black, which converts any oxygen present to water, followed by passage through the walls of an electrically heated palladium tube, which is permeable only to hydrogen.

The oxygen was purified by liquefaction (by immersion in liquid air) and careful fractionation.

The purified gases were then passed into a special explosion apparatus where their volumes were accurately determined after three hours' immersion in a bath of melting ice and at 760 mm. pressure. They were then exploded, the hydrogen being usually in excess. The water formed was frozen by means of a bath of

solid carbon dioxide and acetone (giving a temperature of  $-78^{\circ}$  approximately.) The residual hydrogen was then sucked off through a phosphorus pentoxide tube and its volume accurately measured (again at  $0^{\circ}$  C. and 760 mm. pressure).

Other gases which have been investigated and their composition by volume accurately determined have similarly yielded results very close to, but not exactly, those which would be expected from Gay-Lussac's Law. Thus Gray and Burt (1909) obtained 1.0079 volumes of hydrogen from 2 volumes of hydrogen chloride gas; and Guye and Pintza found the combining ratio of nitrogen and hydrogen in ammonia to be 1 : 3.00172.

The deviations of these values from whole numbers follow from the circumstance already referred to that no gas exactly obeys the simple gas laws, i.e., Boyle's Law and Charles's Law. Furthermore, the magnitudes of these deviations, even when small, are different for different gases. It follows, therefore, that whatever may be the underlying peculiarity of matter which reveals itself in the almost exact generalization of Gay-Lussac's Law, it will not hold with absolute exactness for an arbitrarily assigned pressure and temperature such as those of our Standard Temperature and Pressure must necessarily be; but since Boyle's Law is more closely obeyed at low pressures, Gay-Lussac's Law will also be more nearly exact at very low pressures. The same reasoning which is held to account for the deviations of known gases from the simple gas laws (see Chapter 2) may be taken, therefore, to be the explanation of the non-exactness of Gay-Lussac's Law of Volumes.

In the last chapter the remarkable way in which elements combine by weight was traced to a peculiarity in the constitution of matter; so here it is tempting to make a similar quest. It follows at once (1) that if elements in a gaseous state unite in simple proportions by volume, and (2) that if the elements also unite in simple proportions by atoms, then the number of atoms in equal volumes of the reacting gases must be simply related. J. Dalton concluded that Gay-Lussac's hypothesis required the assumption that equal volumes of the different gases under the same physical conditions contain an equal number—say  $n$ —of atoms. If this were so, when two volumes of hydrogen react with one volume of oxygen to form two volumes of steam,  $2n$  atoms of hydrogen react with  $n$  atoms of oxygen to form  $2n$  "compound atoms" of steam. Hence, two atoms of hydrogen react with one atom of oxygen to form two "compound atoms" of steam. In that case, every atom of oxygen must be split into half an atom to make two "compound atoms" of steam. This contradicts the fundamental postulate of the atomic theory, or Dalton's aphorism: "Thou knowest no man can split an atom," meaning, of course, that atoms are indivisible in chemical reactions. Similar contradictions are encountered in nearly every case of combination between gases, hence Dalton rightly claimed this guess to be an untenable assumption and it is clearly necessary to try another.

## § 2 Avogadro's Hypothesis

A. Avogadro (1811) pointed out that the fallacy in Dalton's reasoning can be avoided if a clear distinction is made between elementary atoms and the small particles of a gas. Avogadro assumed that the small particles of a gas are aggregates of a definite number of atoms, and called these aggregates **molecules** in order to distinguish them

from the ultimate atoms. The term "molecule" is the diminutive form of the Latin word *moles*, a mass. Each molecule of an elementary gas contains the same number and kind of atoms.

Hence, modifying Dalton's guess he suggested that **"equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules."** To illustrate how this helps to resolve the dilemma in which Dalton's suggestion places us, assume that each molecule of hydrogen gas is composed of two atoms of hydrogen, and let us make a similar assumption for oxygen.

Suppose that two volumes of hydrogen contain  $2n$  molecules of hydrogen, then one volume of oxygen will contain  $n$  molecules. These react to form  $2n$  molecules of steam—each molecule of steam contains two atoms of hydrogen and one atom of oxygen. Hence, as W. K. Clifford expressed it, although atoms cannot be split so that one atom of oxygen enters into the composition of two molecules of water, yet one molecule of oxygen can be divided between two molecules of water.

Again, with hydrogen and chlorine, supposing that the chlorine molecule also contains two atoms, then one volume of hydrogen, containing  $n$  molecules, will react with one volume of chlorine, likewise containing  $n$  molecules, to form two volumes of hydrogen chloride, i.e.,  $2n$  molecules each consisting of an atom of hydrogen and an atom of chlorine.

Avogadro thus modified the atomic hypothesis and introduced the conception of two orders of minute particles, (1) the atom as the unit of chemical exchange; and (2) **the molecule or the smallest particle of an element or compound which exists free in a gas.** This definition of a molecule is usually extended into the less satisfactory definition: **A molecule is the smallest particle of an element or compound which exists in a free state;** meaning that the specific properties of a substance depend on the component particles remaining intact. If the molecules be subdivided (or augmented) the substance will no longer have the same specific properties, because the nature of the component particles (molecules) is different.

Avogadro's hypothesis, that is to say, that *equal volumes of all gases at the same temperature and pressure contain the same number of molecules*, has proved to be one of the most suggestive and fruitful hypotheses in the development of chemistry. It has correlated what appeared to be antagonistic and contradictory; it has harmonized what appeared to be discordant and confused, and made Dalton's atomic hypothesis a clear, intelligible, and fertile theory. Nevertheless, although put forward as early as 1811, it was not until 1858, by which time confusion had become so serious as to threaten seriously the progress of chemistry as a science, that Cannizzaro succeeded in bringing Avogadro's hypothesis prominently before chemists; until that time it had either been ignored or misunderstood.

### § 3 The Relative Weights of the Molecules

The absolute density of a gas has been defined (Chapter 3) as the weight of a normal litre of the gas measured under standard conditions. Similarly the relative density of a gas may be defined as that number which represents the ratio of the weight of a given volume of the gas to that of an equal volume of a standard gas measured at the same temperature and pressure. Hydrogen is usually taken as this standard gas since it is the lightest gas known, although air has been so used occasionally. Air is a poor standard on account of the variations in its composition, which, though small, are yet appreciable in matters of this sort.

According to Avogadro's hypothesis, equal volumes of gases contain the same number of molecules, consequently, **the relative density of a gas is proportional to its molecular weight.** For, let  $n$  represent the number of molecules in a volume  $v$  of each of two different gases at the same temperature and pressure (Avogadro's rule), and if the molecules of each gas are alike so that the molecular masses of the one gas can be represented by  $m_1$ , and of the other gas by  $m_2$ , then the mass of the one gas will be  $nm_1$ , and of the other,  $nm_2$ . Let the densities of the two gases be respectively  $D_1$  and  $D_2$ , then, since density denotes the mass of unit volume,  $D_1 : D_2 = nm_1/v : nm_2/v$ ; so that  $D_1 : D_2 = m_1 : m_2$ .

That is to say, the molecular weights of gases are proportional to their relative densities, so that we can determine the molecular weights of gases once we have established a standard for their densities, and hence the numerical relation between relative density and molecular weight. For practical purposes **the molecular weight of a substance** which is equal to the sum of the atomic weights of all the atoms in the molecule (referred to the same standard as atomic weights) **is the ratio of the weight of a molecule of the substance to that of an atom of hydrogen.** It follows that we have here a method which will help us to decide on the values of the atomic weights of elements, which, as we have seen (Chapter 4), is not possible on the basis of Dalton's Theory alone.

Experimental methods for the determination of relative density thus assume considerable importance. Many substances which are solid or liquid at ordinary temperatures can be vaporized at higher temperatures, so that it is also possible to find the relative density of these substances, just as it is for those which are gaseous at ordinary temperatures. The relative density in these circumstances is known as the Vapour Density.

### § 4 Determination of Vapour Density

The relative density of a substance which is gaseous at the ordinary temperature may be determined from a knowledge of its absolute density together with that of hydrogen. The determination of these values is effected by the methods already described (see Chapter 3).

In the case of substances which are solid or liquid at ordinary temperatures, but which can be vaporized without decomposition, these methods cannot be employed on account of the elevated temperatures required. For such substances three methods are available, viz.:

- (i) Dumas's method;
- (ii) Hofmann's method;
- (iii) Victor Meyer's method.

The decision as to which method is to be employed in any particular determination will depend upon the amount of substance available and its other properties, as will be seen from the descriptions of these methods which follow.

### (i) Dumas's Method

This is an extension of the method used to determine the absolute densities of gases by the globe method, and the principle is therefore that of measuring the weight and volume of a vapour at a known temperature sufficiently high to vaporize the substance completely.

A light glass bulb, *A*, Fig. 5.1, between 100 and 200 c.c. capacity is weighed, and from 6 to 10 grams of the compound under investigation are introduced into the bulb. By means of a suitable clamp, *D*, the

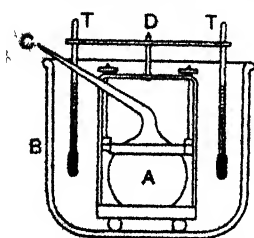


FIG. 5.1.—Dumas's Vapour Density Apparatus

bulb is fixed in a suitable bath, *B*, at a constant temperature  $20^{\circ}$  to  $30^{\circ}$  above the boiling point of the compound under investigation. The compound vaporizes, and when its vapour ceases to issue from the neck, *C*, of the bulb, the tube is sealed at *C* by means of a blowpipe with a small flame. The temperature of the bath at the time of sealing is the average between the two thermometers *T*; the barometric pressure is read at the same time. The bulb is then cooled, cleaned, and weighed. The volume of the bulb is now determined by breaking the

tip, *C*, of the neck under water or mercury, and weighing the bulb when full of liquid.\* The difference between the full and empty bulbs gives the amount of liquid in the bulb. The application of the data can be best illustrated by example.

EXAMPLE.—The following data were obtained for vanadium tetrachloride,  $\text{VCl}_4$ :

Weight of globe filled with air ( $9^{\circ}$ , 762 mm.)	24.4722 grams
Weight of sealed globe ( $9^{\circ}$ , 762 mm.)	25.0102 grams
Temperature of bath when sealing the globe	$215^{\circ}$
Barometer when sealing the globe	762 mm.
Weight of bulb full of water	194 grams

\* If the globe contains residual air, a correction must be made. The volume of the vapour will be equal to the volume of the globe, less the volume of the residual air; and the weight of the vapour will be this difference plus the buoyancy of a quantity of air at *t* and *p* of the second weighing, equal to the volume of the vapour.



The globe held  $194 - 24.4722 = 169.5$  grams of water at  $9^\circ$ . This represents very nearly 169.5 c.c. of water, or the capacity of the globe is 169.5 c.c. The apparent weight of the substance at  $9^\circ$  is  $25.0102 - 24.4722 = 0.538$  gram. The empty globe was buoyed up, during weighing, by its own bulk of air at  $9^\circ$  and 762 mm., and since 1 c.c. of air at N.T.P. weighs 0.001293 gram,  $169.5$  c.c. of air at  $9^\circ$  and 762 mm. weigh at N.T.P.  $(0.001293 \times 169.5 \times 273 \times 762) \div (760 \times 282) = 0.213$  gram. This, added to 0.538 gram, gives 0.751 gram, the weight of the vapour in the globe at the time of sealing. The 0.751 gram of vapour occupied 169.5 c.c. at  $215^\circ$  and 762 mm. pressure, or 95.10 c.c. at  $0^\circ$  and 760 mm. pressure.

Then, since the weight of 1 c.c. of hydrogen at N.T.P. is 0.00009 gram, we have that the vapour density of vanadium tetrachloride

$$= \frac{0.751}{95.1 \times 0.00009} = 87.74$$

Since the vaporization is carried out at atmospheric pressure, it is also necessary to employ fairly high temperatures which makes the method inappropriate for substances which readily decompose; but the vapour does not come in contact with mercury or any confining liquid and so this method can be used for substances, such as bromine, for which such contact must be avoided. By using porcelain or platinum vessels it can also be employed for substances which only volatilize at very high temperatures.

### (ii) Hofmann's Method

This is a modification of an earlier method due to J. L. Gay-Lussac (1811). A known weight of the substance in a small stoppered glass bulb, shown on an enlarged scale at *W*, Fig. 5.2, is taken. The bulb is introduced below a barometer tube filled with mercury, and surrounded with a jacket through which the vapour of a liquid, which boils about  $20^\circ$  above the boiling point of the compound under investigation, is passing. The bulb ascends to the upper level of the mercury, and the substance is thus vaporized under a reduced pressure. When everything is in equilibrium, the volume of the vapour is read; the height of the barometer and the temperature of the apparatus are also read.

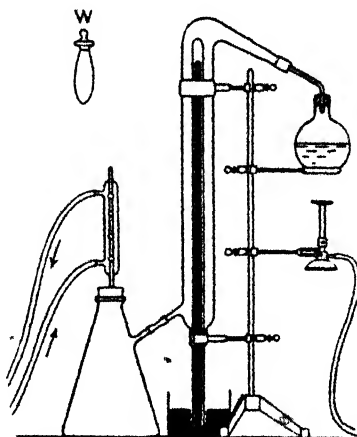


FIG. 5.2.—Hofmann's Vapour Density Apparatus

**EXAMPLE.**—The following data were obtained for carbon tetrachloride,  $\text{CCl}_4$ :

Weight of liquid in bulb	.	.	.	.	0.3380 gram
Volume of vapour	.	.	.	.	109.8 c.c.
Temperature of vapour	.	.	.	.	$99.5^\circ$
Barometer	.	.	.	.	746.9 mm.
Height of mercury in tube	.	.	.	.	283.4 mm.

The pressure of the vapour is the barometric height less the height of the column of mercury in the Hofmann's tube, that is,  $746.9 - 283.4 = 463.5$  mm. Hence, 0.3380 gram of vapour at  $99.5^\circ$  and 463.5 mm. pressure occupies 109.8 c.c. and 49.09 c.c. at  $0^\circ$  and 760 mm.

So that the vapour density of carbon tetrachloride is

$$\frac{0.3380}{49.09 \times 0.00009} = 76.5$$

This method is specially suitable for substances which decompose at or near their boiling points at normal pressure.

### (iii) Victor Meyer's Method

In Victor Meyer's method, an elegant and simple method first described in 1877, the volume of *air* displaced by a known weight of vapour is determined. It can be carried out more easily and quickly than either of the preceding methods, and requires only small quantities of substance. It is therefore widely used.

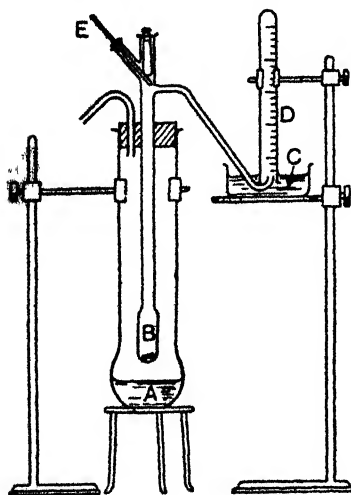


FIG. 5.3.—Victor Meyer's Vapour Density Apparatus

A bulb, *B*—about 200 c.c. capacity—has a long neck fitted with a side tube leading to a pneumatic trough, *C*, Fig. 5.3. At *E* is a side tube through which passes a glass rod so arranged that a small glass bottle—*W*, Fig. 5.2—will rest against it when introduced into the top of the apparatus. The bulb is surrounded as shown by an outer jacket, *A*, containing a liquid which boils at  $20^\circ$  to  $30^\circ$  above the boiling point of the compound under investigation. To make a determination, a weighed quantity of the substance whose vapour density it is required to find is introduced into the small stoppered bottle and placed in the apparatus resting against the glass rod *E*. The liquid in the outer jacket is boiled, and when no more bubbles pass out through the side tube, a graduated tube, *D*, filled with water

is inverted over the side tube. The glass rod, *E*, is partly pulled out so that the small bottle drops into the bulb *B* (which contains a little asbestos or glass wool to break its fall). The substance in the small bottle rapidly vaporizes and drives a stream of air bubbles into the graduated tube. When this stream of bubbles ceases, the tube is carefully transferred to a cylinder of water, and after a time the volume, temperature of the water, and barometric pressure are recorded. Since the volume of air displaced is measured *at room temperature* in the graduated tube it is this temperature and not that of the vapour in *B* which is used in the calculations.

EXAMPLE.—The vapour density of chloroform was determined by Victor Meyer's method and the following data were obtained:

Weight of chloroform used	0.1133 gram
Volume of air collected in graduated tube	22.8 c.c.
Temperature of air collected in graduated tube	15°
Atmospheric pressure	751 mm.
Vapour pressure of water at 15°	13 mm.

The 22.8 c.c. of air collected would occupy  $22.8 \times \frac{273}{288} \times \frac{750-13}{760}$  c.c. at N.T.P.  
 $= 20.96$  c.c.

∴ 20.96 c.c. of chloroform vapour weigh 0.1133 gram.

∴ vapour density of chloroform  $= \frac{0.1133}{20.96 \times 0.00009} = 60.08$

### § 5 The Relation between Vapour Density and Molecular Weight

It was shown on page 77 that the molecular weights of gases are proportional to their relative densities, and that provided the appropriate numerical relationship can be established, the molecular weight of any given gas may be calculated from a knowledge of its vapour density.

The vapour density of a substance has already been defined as the ratio of the weight of a given volume of vapour, under given conditions, to the weight of the same volume of hydrogen under the same conditions. That is, the Vapour Density of a Substance

$$= \frac{\text{Wt. of a certain volume of substance at } t^{\circ} \text{ C. and } B \text{ mm. press.}}{\text{Wt. of same volume of hydrogen at } t^{\circ} \text{ C. and } B \text{ mm. press.}}$$

According to Avogadro's hypothesis, both these volumes contain the same number (say  $n$ ) of molecules. Hence, Vapour Density of Substance

$$= \frac{\text{Wt. of } n \text{ molecules of substance}}{\text{Wt. of } n \text{ molecules of hydrogen}}$$

$$= \frac{\text{Wt. of 1 molecule of substance}}{\text{Wt. of 1 molecule of hydrogen}}$$

But the Molecular Weight of a Substance (page 77)

$$= \frac{\text{Wt. of 1 molecule of substance}}{\text{Wt. of 1 atom of hydrogen}}$$

from which it follows that the Molecular Weight of a Substance = Vapour Density of substance  $\times$  number of atoms in 1 molecule of hydrogen.

For the final solution of our problem it thus becomes necessary to know the number of atoms in the molecule of hydrogen.

We saw at the beginning of the present chapter that since hydrogen and chlorine combine in the proportion of 1 volume of hydrogen to 1 volume of chlorine to form two volumes of hydrogen chloride, the

hydrogen molecule must contain *at least* two atoms of hydrogen. For by Avogadro's hypothesis  $n$  molecules of hydrogen furnish the hydrogen atoms required for  $2n$  molecules of hydrogen chloride. If a single molecule of hydrogen chloride contains *one* atom of hydrogen only, then the molecule of hydrogen must consist of two atoms. If each molecule of hydrogen chloride contains more than one atom of hydrogen then the hydrogen molecule must consist of a multiple of two atoms.

It will be shown in a later chapter (see page 541) that chemical evidence indicates that hydrogen chloride contains but one atom of hydrogen per molecule; hence we conclude that the hydrogen molecule contains two atoms.

Evidence of an entirely different kind confirms this view, for it can be shown that the ratio of the two specific heats of a gas is related to the number of atoms in its molecule.

It will be remembered that "specific heat" is a term employed to represent the amount of heat required to raise the temperature of one gram of a substance  $1^{\circ}\text{C}$ . A gas can be heated by simple compression, its specific heat must then be zero; but a certain amount of energy, equivalent to the specific heat, is needed for the work of compression. Again, a gas, if it be expanded, is cooled; if the cooling effect of expansion just counter-balances the heat added to the gas, the temperature will remain constant; and the specific heat appears to be indefinitely large. Here work, equivalent to the heat supplied, is performed by the expanding gas. These facts show that the condition of the gas must be stated before it is possible to define its specific heat. It is conventionally agreed that if the gas be allowed to expand during a change of temperature so that its pressure remains constant, the amount of heat required to raise the temperature of one gram of the gas  $1^{\circ}\text{C}$ . shall be called the **specific heat under constant pressure**, and symbolized by  $c_p$ . If the pressure be increased so that the volume remains constant when the gas is heated, the amount of heat required to raise the temperature  $1^{\circ}\text{C}$ . is likewise called the **specific heat under constant volume**, and symbolized  $c_v$ .

In the following discussion, it will be remembered that the Kinetic Theory assumes that the temperature is proportional to the average speed of translation of the moving molecules—an increase of the speed is accompanied by a rise of temperature, and conversely. The heat imparted to a gas is not spent merely in raising the temperature of the gas; that is, in speeding up the motions of the molecules. Energy is spent in—

(1) *Augmenting the speed of the moving molecules.*—The heat required actually to increase the kinetic energy of the moving molecules so as to produce a rise of temperature is the same for all gases. Let  $a$  denote this quantity for one gram-molecule of gas.

(2) *Performing external work.*—Heat energy is needed to overcome the pressure of the atmosphere when the gas is allowed to expand. Call this quantity  $b$  for one gram-molecule of gas. Since the coefficient of

thermal expansion of all gases is the same (page 23), this quantity is practically constant for equal volumes, or equimolecular weights.

(3) *Performing internal work.*—Heat energy is required to produce changes within the molecule which may alter the motions or orientation of the constituent atoms of the molecule, or raise the kinetic energy of the atoms moving within the molecule. Let  $c$  denote the energy spent within the molecule per gram-molecule per degree rise of temperature. A certain amount of energy must also be spent in overcoming the effects of intermolecular attractions (page 42). This can be neglected for the time being.

The ratio of the two specific heats may now be written:

$$\frac{C_p}{C_v} = \frac{a + b + c}{a + c}$$

where, for one gram-molecule,  $C_p$  is the specific heat at constant pressure, and  $C_v$  the specific heat at constant volume.

**The specific heat of a gas at constant volume.**—We have seen (page 37) that  $pv = \frac{1}{2}mu^2$  where  $m$  denotes the mass, and  $u$  the average velocity of the molecules. But the kinetic energy of a body of mass  $m$  moving with a velocity  $u$  is  $\frac{1}{2}mu^2$ ; hence since  $pv = \frac{2}{3} \times \frac{1}{2}mu^2$  the kinetic energy of the molecular motions is  $\frac{3}{2}pv$ . But  $pv = RT$  (page 26). Hence the kinetic energy of molecular motion is  $\frac{3}{2}RT$ . If one gram-molecule of gas be heated through  $1^\circ \text{C.}$ , the kinetic energy becomes  $\frac{3}{2}R(T + 1)$ . Hence at constant volume, the thermal value of the increased kinetic energy is  $\frac{3}{2}R(T + 1) - RT = \frac{3}{2}R$  cal. Hence the specific heat of the gas at constant volume, i.e.,  $C_v = \frac{3}{2}R + c$ .

**The external work done by an expanding gas.**—Again, if a gram-molecule of gas expands against atmospheric pressure when its temperature is raised  $1^\circ \text{C.}$ , the gas, in consequence, does work by pressing back the atmosphere, so to speak. The equivalent of this work must be supplied in the form of heat. This work is equivalent to the product of the pressure times the change in volume. Let  $x$  denote the change in volume when the gas is heated  $1^\circ \text{C.}$ , under a constant pressure; then,  $p(v + x) = R(T + 1)$ , and  $pv = RT$  (page 26). By subtraction  $px = R$ . This means that when a gram-molecule of gas is heated  $1^\circ \text{C.}$ , the resulting expansion against atmospheric pressure does work equivalent to  $R$  cal.

**The specific heat at constant pressure.**—Hence,  $R$  cal. must be added to the previous result to obtain the thermal equivalent of the energy supplied to one gram-molecule of gas in the form of heat when its temperature is raised  $1^\circ$ . Therefore the specific heat of the gas at constant pressure, i.e.,  $C_p = \frac{5}{2}R + c$ .

From these results we can evaluate the ratio of the two specific heats (usually denoted by the symbol  $\gamma$ ) for

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + c}{\frac{3}{2}R + c}$$

The value of  $c$  will vary for different gases, for it is related to the molecular complexity of the gas, and for a monatomic gas it may be expected to be zero. When  $c = 0$  we then have

$$\gamma = \frac{5}{3} = 1.667.$$

Experimental determinations of the value of  $\gamma$  for various gases show that the maximum value so far found is 1.667 and that the remaining values fall into fairly well-defined groups, as can be seen from the following table:

TABLE III.—RATIO OF THE TWO SPECIFIC HEATS OF GASES

Gas	Mole- cule	Atoms per mole- cule	$\gamma$	Gas	Mole- cule	Atoms per mole- cule	$\gamma$
Mercury . . .	Hg	1	1.67	Hydrogen sulphide	H <sub>2</sub> S	3	1.34
Argon . . .	A	1	1.67	Ammonia . . .	NH <sub>3</sub>	4	1.34
Hydrogen . . .	H <sub>2</sub>	2	1.41	Nitrous oxide . .	N <sub>2</sub> O	3	1.32
Nitrogen . . .	N <sub>2</sub>	2	1.41	Methane . . .	CH <sub>4</sub>	5	1.31
Oxygen . . .	O <sub>2</sub>	2	1.40	Carbon dioxide . .	CO <sub>2</sub>	3	1.30
Carbon monoxide	CO	2	1.40	Ethylene . . .	C <sub>2</sub> H <sub>4</sub>	6	1.26
Hydrogen chloride	HCl	2	1.39	Ethane . . .	C <sub>2</sub> H <sub>6</sub>	8	1.22
Chlorine . . .	Cl <sub>2</sub>	2	1.32	Alcohol . . .	C <sub>2</sub> H <sub>5</sub> OH	9	1.13
Bromine . . .	Br <sub>2</sub>	2	1.29	Benzene . . .	C <sub>6</sub> H <sub>6</sub>	12	1.09
Iodine . . .	I <sub>2</sub>	2	1.29	Turpentine . . .	C <sub>10</sub> H <sub>16</sub>	26	1.03
Iodine chloride .	ICl	2	1.31	Ether . . .	C <sub>4</sub> H <sub>10</sub> O	15	1.02

There is thus a group of gases for which  $\gamma$  is round about 1.65, another for which it is approximately 1.4, and so forth. There is no gas for which the value is much above 1.4 unless it is about 1.65, the theoretical value for a monatomic gas. It seems, therefore, reasonable to conclude that gases for which  $\gamma$  is 1.4 are diatomic, especially as when applied this conclusion is found to be in agreement with the chemical evidence.

Thus, the ratio of the two specific heats of hydrogen being 1.41 we have confirmation for the view that the hydrogen molecule contains two atoms.

Hence, resuming the discussion of the relation between vapour density and atomic weight, we have, as has been shown,

Mol. Wt. = Vap. Density  $\times$  No. of atoms in 1 molecule of hydrogen, and accordingly:

$$\text{Molecular Weight of a Substance} = 2 \times \text{Vapour Density.}$$

### § 6 The Gram-molecular Volume of a Gas at N.T.P.

We are now in a position to calculate another important constant, viz., the volume occupied at standard temperature and pressure by a gram-molecular weight (i.e., the number of grams of gas numerically

equal to the molecular weight) of any gas. Avogadro's Hypothesis shows us that this volume will be the same for all gases, so that if we calculate this value for one gas we shall, theoretically, know its value for all other gases.

The molecular weight of hydrogen has been shown to be twice its atomic weight. Hydrogen was formerly taken as the standard of atomic weight and hence its atomic weight was put at unity. But, as will be explained in Chapter 7, it is now usual to take oxygen as the standard element with an atomic weight of 16. The atomic weight of hydrogen then becomes 1.008 and its molecular weight 2.016 in consequence.

Hence a gram-molecular weight of hydrogen = 2.016 grams.

The density of hydrogen is 0.09 gram per litre at S.T.P.

∴ 1 gram-molecular weight of hydrogen occupies  $\frac{2.016}{0.09} = 22.4$  litres at S.T.P.

Now consider another gas of molecular weight  $M$

$$\text{Since } M = \frac{\text{Weight of 1 molecule of substance}}{\text{Weight of 1 atom of hydrogen}}$$

$$\begin{aligned} \text{Weight of 1 molecule of substance} \\ = M \times \text{Weight of 1 atom of hydrogen.} \end{aligned}$$

1 gram-molecular weight of substance weighs  $M$  grams,

∴  $M$  grams of substance contain

$$\begin{aligned} & \frac{M}{M \times \text{weight of 1 atom of hydrogen}} \text{ molecules} \\ &= \frac{1}{\text{Weight of 1 atom of hydrogen}} \text{ molecules.} \end{aligned}$$

That is to say, the gram-molecular weights of all gases contain the same number of molecules. Therefore, the gram-molecular weight of any gas at S.T.P. will occupy the same volume as 2.016 grams of hydrogen, that is, 22.4 litres.

This is a very important fact, and it can be used in calculating molecular weights, for if the weight of 22.4 litres of a gas of unknown molecular weight be determined, its gram-molecular weight, which is numerically equal to its molecular weight, is known. The results of the typical vapour density experiments given on pages 78–81 could have been used in this way to evaluate the molecular weights of the several substances.

## § 7 The Avogadro Number

It has just been shown that the number of molecules in a gram-molecular weight of any gas at S.T.P. is a constant. This constant is usually denoted by the symbol  $N$ , and is called Avogadro's Constant

or the Avogadro Number. Its value has been found by several independent methods with results so concordant as to furnish very strong support indeed for the Molecular Theory. The accepted value is  $6.023 \times 10^{23}$ .

The most direct method is that due to Rutherford and Geiger, who counted the number of  $\alpha$ -particles emitted from radium (see Chapter 10) in a given time, and collected the helium produced by a large quantity of radium in a long period. Since each  $\alpha$ -particle becomes a helium atom, this gives a means of calculating the Avogadro Number.

Other methods which have been employed are based on the study of the Brownian movement (see Chapter 19, page 280), the determination of the charge of the electron (see Chapter 10, page 135) and the diffraction of X-rays by crystals (page 197).



## CHAPTER 6

# EQUIVALENT WEIGHTS

Since it is already settled for us by custom that quantities of different substances are to be called equal when or because they are equivalent gravimetrically, we have no choice but also, from the chemical point of view, to call those quantities of substances equal which interact in single chemical changes.—E. DRIVERS, 1902.

### § 1 Definition of Equivalent Weights of Substances

IN Chapter 4 (page 66) the quantity known as the Combining Weight or Equivalent Weight of an element is defined as the number of parts by weight of an element which combine with, or replace, eight parts by weight of oxygen, or the combining weight of any other element.

Some such conception as that of the equivalent weight was in the minds of chemists quite early in the "modern" period of the subject. Thus Cavendish in 1766 called a given weight of potash the equivalent of another (different) weight of lime if both were able exactly to neutralize the same weight of an acid. In 1788 he demonstrated that the quantities of nitric and sulphuric acids which neutralized two identical weights of potash would also decompose identical weights of marble—different in weight, of course, from the potash. This seems to have been the first clear recognition of the principle of equivalents as understood chemically, and pre-dated Dalton's Atomic Theory (of which it is a logical consequence) by some fifteen years.

The generalization of these results is due to J. B. Richter who, in 1792, published a table of equivalent weights of acids and bases.

This early work is a reminder that the conception of equivalents is not confined to elements, but applies also to compounds, that is to say, to any pure substance which is able to enter into a chemical reaction. This is an important matter in volumetric analysis which depends upon the use of solutions of known concentration. The standard adopted for the concentrations of such solutions is that known as a **normal** solution, which is defined as a **solution which contains the gram-equivalent weight of a substance in a litre of solution**. The gram-equivalent weight is the number of grams of the substance numerically equal to the equivalent weight.

The equivalent weight of any pure substance is defined in the first instance as that weight of it which combines with, or replaces, the equivalent weight of hydrogen. Since the molecule of hydrogen consists of two atoms, its equivalent weight will be half its molecular weight. Hence, since (page 85) the gram-molecular weight of hydrogen

occupies 22.4 litres at S.T.P., the gram-equivalent weight of hydrogen will occupy 11.2 litres at S.T.P.

Further, as a normal solution is one which contains a gram-equivalent weight in one litre of solution, one litre of the solution will react with the gram-equivalent weight of any other substance with which it is capable of entering into a reaction.

We thus arrive at the following comprehensive definition: **The gram-equivalent weight of a substance is that weight of it which will combine with or displace 11.2 litres of hydrogen (measured at S.T.P.) or 8 grams of oxygen, or the known equivalent weight of any other element or react with 1 litre of any normal solution.**

In accordance with this definition the following definitions are sometimes employed in particular cases:

(a) The equivalent weight of an **acid** is that weight of it which contains one equivalent weight of replaceable hydrogen.

(b) The equivalent weight of an **oxidizing agent** is that weight of it which contains one equivalent weight (i.e., 8 parts by weight) of *available* oxygen.

## § 2 The Determination of Equivalent Weights

It is evident that the determination of the equivalent weights of the elements is of fundamental importance, both on account of their practical use in all quantitative, and particularly analytical, operations, and also on account of their being, as will be seen in the next chapter, the basis for the determination of Atomic Weights.

The different methods available for the determination of equivalent weights may be summarized under the following heads:

- (i) Hydrogen displacement.
- (ii) Oxide methods.
- (iii) Chloride methods.
- (iv) Replacement methods.
- (v) Electrolysis.
- (vi) Conversion methods.

## § 3 Equivalent Weight by Hydrogen Displacement

This method can be used for those metals which readily liberate hydrogen from dilute solutions of mineral acids or of alkalis. Thus it can be employed to determine the equivalents of zinc, iron and magnesium by the action of these metals with dilute hydrochloric acid; of aluminium by its action with either dilute hydrochloric acid or sodium hydroxide solution. The method can also be modified so as to apply to sodium, by allowing it to react with alcohol, from which it displaces hydrogen easily and smoothly. It is evident, however, that the method of hydrogen displacement can only be used for the determination of the equivalent weight of a limited number of metals.

The method may be explained by reference to Fig. 6.1.

The apparatus consists of a measuring tube and a levelling tube containing water, connected by rubber tubing as shown. The flask contains dilute acid (or alkali or alcohol, as above) and a small tube is suspended in it containing a weighed quantity of the metal whose equivalent is to be determined. To perform the experiment the levelling tube is raised until the surface of the water in the measuring tube is at zero, and at the same level as the water in the levelling tube, the flask being detached while this is being done. The flask is now attached to the apparatus, the levelling tube is raised or lowered until the water-levels in both tubes are the same, and the position of the level in the measuring tube is read. The flask is then tilted so that the metal comes in contact with the acid, and the levelling tube is lowered at the same time. When all the metal has dissolved, and the apparatus has had time to cool to room temperature, the levels in the two tubes are again made the same. The position of the water-level in the measuring tube is then read, thus giving the volume of hydrogen which has been liberated. The height of the barometer is then found, and the temperature of the room noted. The volume of hydrogen is then corrected to S.T.P., allowance being made for the pressure of aqueous vapour, since the moist gas has been measured (see pages 38-41). The volume of hydrogen at S.T.P. liberated by a known weight of metal is now known, whence the equivalent of the metal can be calculated since 1 litre of hydrogen at S.T.P. weighs 0.09 gram; or put in another way, since the equivalent of hydrogen occupies 11.2 litres at S.T.P.

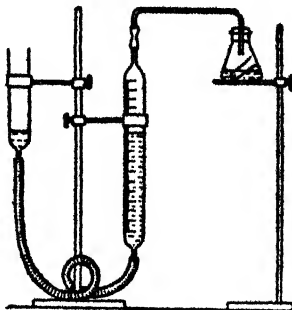


FIG. 6.1.—Hydrogen Displacement Method

#### § 4 Oxide Methods

Methods for finding the equivalent weight of an element involving the use of the oxide may be subdivided thus:

- (a) direct oxidation (direct synthesis);
- (b) indirect oxidation (indirect synthesis);
- (c) reduction of the oxide (analysis).

##### *Direct Oxidation*

The exact procedure to be followed depends upon the nature both of the element and of its oxide. Where a solid element burns reasonably slowly to a solid oxide, the conversion may be carried out in a crucible. If a gaseous oxide is formed, as in the case of carbon, a suitable means of discovering the weight of the oxide must be devised.

For gaseous elements like hydrogen, a special technique has to be employed and much ingenuity has been expended in coping with this problem. (See Chapter 7 for an account of the determination of the hydrogen-oxygen ratio.)

The method may be illustrated by experiments with calcium and with carbon.

The equivalent weight of calcium may be found by placing in a weighed crucible a known weight of calcium turnings and heating gently until the calcium burns, continuing the heating until all the action is over. The crucible is then allowed to cool and a few drops of water are added from a pipette,\* the addition being made very carefully so as to avoid any loss due to the vigour of the reaction which takes place. The crucible is then heated again, at first gently, and then strongly, after which it is allowed to cool in a desiccator, and reweighed. It is then repeatedly reheated, cooled and reweighed until a constant weight is attained.

From these weighings the weight of oxygen which has combined with a known weight of calcium is known. Hence the weight of calcium which would combine with eight grams of oxygen (i.e., the equivalent weight of calcium) can be calculated.

This method is sometimes recommended for the determination of the equivalent of magnesium, but it is not completely satisfactory for this metal for the following reasons. First, it is very difficult to prevent loss of magnesium oxide in the form of fumes; second, the magnesium attacks the lining of the crucible; and third, the weight of magnesium used is small and so relatively large errors are incurred in the still smaller weight of oxygen.

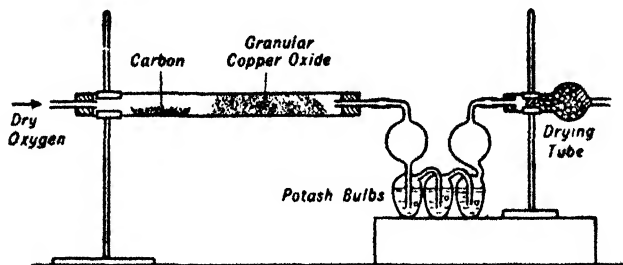


FIG. 6.2.—Equivalent Weight of Carbon

The diagram (Fig. 6.2) illustrates, in simplified form, the apparatus employed by Stas to find the equivalent of carbon. A silica boat containing a weighed quantity of pure dry carbon is heated in a current

\* Strictly speaking, in this case, the oxidation is partly direct and partly indirect. The calcium combines to some extent with the nitrogen of the air as well as with the oxygen, and water is added to convert the nitrogen compound so formed into the oxide.

of pure dry oxygen, and the carbon dioxide formed is absorbed in potash bulbs, containing a strong solution of potassium hydroxide, which are weighed before and after the experiment. The drying tube is weighed along with the potash bulbs, since its function is to prevent water vapour being carried out of the apparatus by the stream of oxygen passing through it. The tube in which the boat is heated is packed with dry granular copper oxide, which is heated before the carbon in the boat is allowed to burn. This is done to ensure complete conversion to carbon dioxide, since any carbon monoxide formed would not be absorbed by the potassium hydroxide solution; should any carbon monoxide be formed it would be converted into carbon dioxide by the hot copper oxide (see Chapter 20).

The loss in weight of the boat and contents in the experiment gives the weight of carbon burned, while the increase in weight of the potash bulbs gives the weight of carbon dioxide formed. Hence the equivalent of carbon can be calculated.

The equivalent weight of sulphur can be found in a similar manner, the use of copper oxide being unnecessary, however, in this case.

#### *Indirect Oxidation*

This method has to be employed when the required oxide is not formed by heating the element in air or oxygen. Examples of the application of this method are furnished by copper and tin.

With either of these metals conversion into the oxide can only be superficially effected by direct oxidation, but can easily be brought about indirectly by means of nitric acid. A weighed quantity of the metal is treated with a slight excess of somewhat diluted nitric acid and, after the first action has subsided somewhat, is warmed gently, and finally evaporated to dryness, care being taken to avoid loss. The dry residue is then heated strongly to constant weight. Copper, zinc, lead and magnesium are converted by this process, first, into their nitrates (see pages 452, 689), and then by strong heating into the oxides. Tin does not form a nitrate, but an insoluble white compound, meta-stannic acid, results (see page 785) which, when strongly heated, loses water, leaving stannic oxide.

Experiments such as these give the weight of oxide formed from a known weight of metal, from which the equivalent weight of the metal can be calculated.

#### *Reduction of the Oxide*

In this method the principle is the exact converse of the two preceding ones. In them a known weight of metal is converted, directly or indirectly, into the oxide whose weight is found. In the present method, a known weight of oxide is reduced to the metal. The method is applicable to those elements whose oxides are reduced at a moderate temperature by the action of hydrogen, or carbon monoxide (or coal-gas).

The process may be exemplified again by reference to copper, and is illustrated by Fig. 6.3.

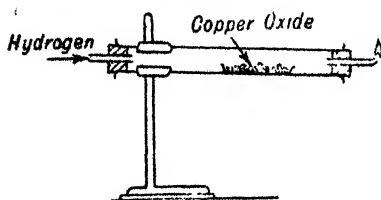


Fig. 6.3.—Equivalent of Copper

A weighed quantity of dry copper oxide is placed in a porcelain or silica boat in a hard glass tube arranged as in the diagram. Hydrogen is passed through the tube until all the air has been expelled and is then lighted at the jet as shown. The tube in the neighbourhood of the boat is then heated, at first gently

and then more strongly until the reduction appears to be complete. The tube is then allowed to cool with the stream of gas still passing, the boat transferred to a desiccator and reweighed. The process is repeated until a constant weight is obtained.

The calculation of the equivalent weight is carried out in the same way as in the two previous methods.

### § 5 Chloride Methods

The determination of equivalent weights by way of the chlorides of elements is one of the methods employed very widely in the most accurate atomic weight work (see Chapter 7, page 104). It depends upon the fact that silver chloride is practically insoluble and that silver can be readily obtained in a high degree of purity. Also a very large number of elements form soluble chlorides which can be prepared in a high degree of purity. The equivalent weights of chlorine and silver are known very accurately and the extent of the very slight solubility of silver chloride is also known. Hence the method is one of wide application and capable of a high order of accuracy.

The procedure may be illustrated by the following simple experiment. A small quantity of pure dry sodium chloride is weighed out on a small watch glass and then carefully transferred to a clean beaker, the last particles of salt being washed into the beaker by means of distilled water from a wash-bottle, and sufficient distilled water is added to dissolve all the salt completely. A little dilute nitric acid is also added. Silver nitrate solution is then added carefully, and a precipitate of silver chloride is formed. Silver nitrate solution is added until no further precipitate results on the addition of another drop of solution. The precipitate is then filtered off on a weighed filter paper or Gooch crucible (see below), care being taken to transfer every particle of precipitate to the paper and to wash thoroughly with distilled water until no soluble salts remain. The filter paper and precipitate are then dried in a steam oven and reweighed.

The calculation of the equivalent weight from such an experiment is best illustrated by means of an example. In an experiment 0.6215

gm. of sodium chloride gave 1.5236 gm. of silver chloride. The equivalent weight of silver is 107.88 and that of chlorine 35.46. Hence if  $E$  is the equivalent of sodium we have

$(E + 35.46)$  gm. of sodium chloride give  $(107.88 + 35.46)$  gm. of silver chloride.

$$\therefore \frac{E + 35.46}{143.34} = \frac{0.6215}{1.5236}$$

$$\therefore E = 23.01.$$

### *The Gooch Crucible*

This consists of a crucible of the shape shown in Fig. 6.4, having the base pierced by a number of fine holes. By pouring into the crucible a suspension of finely ground purified asbestos in distilled water, a thin pad of asbestos is formed over the bottom of the crucible. The crucible prepared in this way is then dried and weighed and is ready for the filtration of a precipitate. Filtration is effected by means of gentle suction, using the apparatus shown in Fig. 6.4.

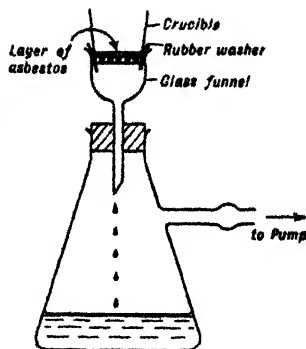


FIG. 6.4.—Gooch Crucible in use

## § 6 Replacement Methods

This method depends upon the fact that some metals such as zinc, which are high in the electro-chemical series (see page 231), will displace those lower in this series from solutions of their salts. A familiar example of this is the "plating" of the blade of a steel pen-knife with copper by dipping the blade into a solution of copper sulphate (see page 650). The determination of equivalent weights by this method depends upon a knowledge of the equivalent weight of either the displacing or the displaced element, from which the equivalent weight of the other can be calculated from a knowledge of the weight of one element displaced by a known weight of the other.

The exact procedure to be followed will depend upon the particular element being displaced, but in general differs only in detail from the following.

A known weight of zinc foil is added to excess of copper sulphate solution contained in a porcelain dish, and the solution warmed slightly. The surface of the foil will be seen to become coated with copper, but by tapping it with a glass rod the copper can be made to flake off. In time all the zinc will have disappeared and a precipitate of copper will have been formed. This precipitate is very carefully transferred to a tared filter paper, great care being taken to remove all the particles of copper from the dish to the filter paper. The precipitate is then washed with distilled water until the washings no longer

give a blue colour with ammonia solution (see page 655), and then with a little alcohol. The precipitate is then dried in a steam oven to constant weight.

Theoretically, this method can also be employed with suitable modification for the determination of the equivalent weights of silver, lead, mercury and gold, all of which are displaced quantitatively from solutions of their salts when treated with metallic zinc. In actual practice the method is not of wide application.

### § 7 Equivalent Weight Determination by Electrolysis

As a result of his experiments on the conduction of electricity through solutions of electrolytes, Faraday in 1834 was led to formulate two Laws of Electrolysis (see page 216). The second of these laws, which states that "when the same current is passed for the same time through solutions of several electrolytes in series the masses of each substance liberated are proportional to their chemical equivalents," furnishes a method for finding the equivalent weights of some elements.

It will be seen in Chapter 15 that the passage of a current of electricity through slightly acidified water brings about the liberation of hydrogen at the cathode; and similarly with a solution of copper sulphate, copper is deposited on the cathode. It is thus possible to use the process of electrolysis to find the equivalent weight of copper.

To do this an apparatus for the electrolysis of acidulated water is so arranged that the hydrogen evolved from the cathode may be collected and measured accurately, and is connected in series with an apparatus for the electrolysis of copper sulphate solution, and with a suitable variable resistance and an ammeter. The plate forming the negative plate (or cathode) of the copper apparatus is cleaned and carefully weighed before and after the experiment. A current of about 0.01 ampere is used, a small value being necessary in order to ensure the formation of a compact deposit of copper. The current is allowed to pass until 50 to 100 c.c. of gas have been collected. The increase in weight of the copper cathode is determined after washing and careful drying, and the volume of hydrogen liberated is measured and corrected to S.T.P. The quantities of hydrogen and of copper liberated by the same current are thus known, from which the equivalent of copper can readily be calculated.

### § 8 Conversion Methods

As will be seen in Chapter 7, the determination of the atomic weight of an element usually begins by an accurate determination of its equivalent weight, which latter quantity is generally found by some form of conversion method. The chloride method of finding equivalent weights considered on page 92 is an example of a conversion method and is one very frequently employed. Other examples would be the



conversion of an oxide into its chloride, or other salt; a chloride may be converted into a sulphate; or a chlorate into a chloride. A definite weight of one compound is taken and the weight of the new compound into which it is converted is found. For the subsequent calculation of the equivalent weight, certain fundamental equivalent weights must be known, such as those of chlorine, silver, etc. The process of calculation is similar to that explained on page 93.

The experiments outlined in this chapter, illustrating the various methods available for finding equivalent weights, have been described in a relatively simple form in which they might be carried out by a careful student in any reasonably equipped laboratory. We shall see in the next chapter how these same methods, in the hands of the great masters of quantitative chemistry, have been made capable of yielding results of the highest accuracy, and so form the basis of our accepted values for the Atomic Weights of the elements.

## CHAPTER 7

### ATOMIC WEIGHTS

Every chemical element is regarded as having a distinct nature of its own, which nature, moreover, determines all its activities.—B. P. BROWNE.

#### §1 Atomic Weights and the Atomic Theory

WE have seen in Chapter 4 that the Atomic Theory as enunciated by Dalton suffered from one major defect, viz., that although it gives a definition of an atom as the smallest particle of an element which can enter into, or be expelled from, chemical combination, it does not help us to decide what the smallest combining weight is. The sort of difficulty which arises in attempting to fix the relative weights of the atoms was also pointed out in regard to the element carbon (see page 69). As was then shown, the root of the difficulty is the uncertainty as to the number of atoms entering into combination.

Dalton himself had made the purely arbitrary assumption that when only one compound of two given elements was known, it was considered to be compounded of one atom of each. As was only to be expected, this unwarranted assumption soon led to confusion, and, coupled with the lack of any clear distinction between atoms and molecules, brought about a state of affairs in which, for the time being, almost all attempts to fix the relative weights of the actual atoms was abandoned, and attention was concentrated on combining weights or equivalent weights.

The solution of the problem was indicated by Avogadro in 1811, but it was not until 1858 when Cannizzaro showed how Avogadro's hypothesis could be applied to it that the confusion and difficulty was finally removed.

It is important to notice, before proceeding further, that what is termed the atomic weight of an element is a relative weight. The *absolute* weights of the atoms, although now known with a fair degree of accuracy, do not concern us here, but only the *relative* weights of the atoms of the different elements. For practical purposes this involves the fixing of an arbitrary standard, which was at one time based on hydrogen as unity; but is now taken from oxygen = 16 (page 103).

#### § 2 Atomic Weight from the Molecular Weight of Volatile Compounds by Cannizzaro's Method

Referring back to the difficulty in fixing the atomic weight of carbon from the ratio of the weights of carbon and oxygen in carbon dioxide, we saw that the problem is essentially to determine the

number of atoms of each element contained in one molecule of the compound.

In Chapter 5 it was shown that by means of vapour density measurements it is possible to find the molecular weights of volatile compounds. Furthermore, by way of ordinary chemical analysis the proportions in which the constituents are combined can be determined. Neither of these measurements implies *a priori* any views as to the number of atoms in the molecules of the compounds in question.

Now suppose, in the case of carbon, that by processes such as these the composition of a number of volatile carbon compounds, their vapour densities and molecular weights have been found. Then, as in Table IV, the amount of carbon per molecule in each compound can be calculated.

TABLE IV.—MOLECULAR WEIGHTS OF SOME CARBON COMPOUNDS

Volatile compound of carbon	Composition by weight	Molecular weight	Amount of carbon per molecule
Carbon monoxide .	Carbon 12; oxygen 16	28	12
Carbon dioxide .	Carbon 12, oxygen 32	44	12
Methane .	Carbon 12; hydrogen 4	16	12
Ethylene .	Carbon 24, hydrogen 4	28	$12 \times 2 = 24$
Propylene .	Carbon 36, hydrogen 6	42	$12 \times 3 = 36$
Carbon disulphide .	Carbon 12; sulphur 64	76	12

The smallest weight of carbon in a molecular weight of any of its known compounds is 12, and consequently this number is assumed to be the atomic weight of carbon. The atomic weights of a great number of the elements have been decided in a similar manner.

The actual method used in finding the atomic weight of an element thus involves:

(1) An exact analysis of a compound containing the given element; and consequently the compound investigated must be one which lends itself to exact analysis.

(2) The compound must be one which can be prepared in a highly purified condition.

(3) The compound must be volatile without decomposition, so that its vapour density can be determined.

(4) The compound must contain the smallest proportion of the element under investigation. This matter may need further amplification.

It is important to examine as large a number of volatile compounds as possible when fixing the atomic weight of an element. If only a small number of compounds be examined, there is always a possibility, and perhaps a probability, that the actual minimum weight does not occur amongst the set of compounds taken. It follows, therefore, that the **atomic weight of an element is the least amount of that element**

present in one molecular weight of all its known volatile compounds. The value so obtained is the maximum possible value; the real value may afterwards prove to be a submultiple of this. The atomic weight must be a whole multiple or submultiple of its combining weight. Owing to the fact that the molecular weights of so many volatile compounds of carbon are known it is not very probable that the atomic weight of carbon is less than 12.

This method of fixing atomic weights is due to Cannizzaro (cf. Chapter 5).

### § 3 Dulong and Petit's Rule

P. L. Dulong and A. T. Petit (1819) in their study of the specific heats of different solid elements obtained a remarkable result. They found: The product of the atomic weight,  $A$ , and the specific heat,  $c$ , of an element has nearly always approximately the same numerical value—6.3—Dulong and Petit's rule. This means that the atomic heats or the thermal capacity of the atoms of the elements are approximately the same. The relation is usually expressed:

$$\text{Atomic heat} = Ac = 6.3$$

In illustration, a few elements may be selected at random from a list containing nearly fifty elements for which data are available:

TABLE V.—ATOMIC HEAT OF ELEMENTS

Element	Specific heat	Atomic weight	Atomic heat
Lithium . . . .	0.9408	6.94	6.53
Silver . . . .	0.0559	107.88	6.03
Gold . . . .	0.0304	197.0	6.25
Copper . . . .	0.0923	63.54	5.86
Bismuth . . . .	0.0305	209.0	6.34
Lead . . . .	0.0309	207.21	6.41
Aluminium . . . .	0.2240	26.98	6.04
Iron . . . .	0.1098	55.85	6.12
Uranium . . . .	0.0277	238.07	6.59

The atomic weights here range from 6.94 to 238.07, and yet, when multiplied by the respective specific heats, the products are nearly constant. It has since been deduced from the Kinetic Theory (with certain additional assumptions) that the Atomic Heat of a solid element should be 6 calories per gram-atom per degree Centigrade, which confirms the validity of Dulong and Petit's empirical result. The observed divergencies are the result of disturbing effects which are not taken into account in the theoretical deduction.

This important generalization holds for a great many elements, though there are some important exceptions such as carbon, silicon, boron and beryllium. (The behaviour even of these, however, approximates more closely to Dulong and Petit's Rule at high temperatures.) It can be applied to the computation of the approximate

atomic weight of any solid element whose specific heat is known, and therefore takes its place alongside vapour density measurements as one means by which atomic weights have been determined.

#### § 4 Atomic Weight (exact) from Equivalent Weight and Approximate Atomic Weight

The value for the atomic weight obtained by the application of Dulong and Petit's Rule is clearly only approximate. Similarly, it is not as a rule possible to determine vapour densities and hence molecular weights very accurately. Hence although the percentage composition of a compound can be found with a high degree of accuracy, the atomic weight calculated by the method of § 2 may be only approximate. In contrast, the equivalent weight, like the percentage composition, can be found very accurately indeed. Thus if we can establish the relation between equivalent weight and atomic weight (for clearly they must be very closely related since the equivalent weight is a measure of the relative combining weight of the element and combination takes place between atoms), we shall be able to use our knowledge of the accurate value of the equivalent weight to correct the approximate value of the atomic weight found as above, and so find the atomic weight accurately.

Evidence of the kind referred to on pages 82, 541, makes it extremely probable that (with the exception of hydrazoic acid  $\text{HN}_3$ ) one hydrogen atom rarely, if ever, combines with more than one atom of any other kind. Now consider the case of an element which combines with hydrogen. Let the equivalent weight of the element be  $e$  and its atomic weight  $a$ . Since, by definition, the equivalent weight of the element is the amount which combines with one part by weight of hydrogen, it follows that if the compound contains one atom of the element united with *one* atom of hydrogen  $e = a$ .

Similarly, if the compound contains the atom of the element combined with two atoms of hydrogen, then,

$$e = \frac{a}{2}$$

and, in general, if the hydrogen compound contains  $V$  atoms of hydrogen to one of the element,

$$e = \frac{a}{V}$$

Now since  $V$  is the number of hydrogen atoms, and an atom is indivisible (chemically), it follows that  $V$  must be a small whole number, whence,

Atomic weight = Equivalent weight  $\times$  Small whole number.

This small whole number which represents in the simplest case the number of hydrogen atoms with which an atom of another element

can combine, is called the **valency** of the element and is defined as follows:

**The valency of an element is a number which expresses how many atoms of hydrogen, or of other atoms equivalent to hydrogen, can unite with one atom of the element in question.**

We can now rewrite the expression above in the form:

$$\text{Atomic weight} = \text{Equivalent weight} \times \text{Valency}$$

$$\text{or} \quad \frac{\text{Atomic weight}}{\text{Equivalent weight}} = \text{Valency}$$

We have now established the relation which we set out to find at the beginning of this section by which to correct an approximate value for an atomic weight, found by means of vapour density or specific heat measurements. We now see that the accurate atomic weight must be an exact multiple of the equivalent weight, and we can use methods such as the above, or the others which follow, in order to determine the value of this multiple.

An example will serve to illustrate this conclusion and make the point quite clear.

Indium chloride contains 51.90 per cent of indium. The equivalent of indium is therefore 38.26. The valency of indium was at one time thought to be 2 and the atomic weight would then be 76.52. The specific heat of the metal was found to be 0.057. Hence  $6.4 \div 0.057 = 112.3$ . Now  $112.3 \div 37.8 = 2.97$ .  $\therefore$  The valency of indium is 3 and the atomic weight will be  $38.26 \times 3 = 114.78$ , which is a number close to that adopted for the atomic weight of this element.

It must be noted that some elements combine together in more than one proportion, so forming different compounds. The relation between the proportions in which the combining elements are present in the several compounds is of the kind given by the Law of Multiple Proportions (page 64). It thus follows from our definition of the equivalent weight of an element that a given element may have more than one equivalent weight. Thus, for example, two oxides of copper are known, in one of which 31.77 grams of copper are combined with 8 grams of oxygen; whilst in the other, 63.54 grams of copper are united to 8 grams of oxygen. Therefore, the equivalent weight of copper is 31.77 in the first case, and 63.54 in the second.

In a similar way an element may have three (or more) equivalents according to the number of different compounds which it can form with another given element. But any one element can only have one atomic weight, and accordingly from the relation,

$$\frac{\text{Atomic weight}}{\text{Equivalent weight}} = \text{Valency}$$

such elements as we have been discussing must have more than one value for the valency. Such elements are said to possess *variable valency*.

### § 5 Other Methods for Finding Atomic Weights

The discussion of the previous section reveals the importance of methods for finding the atomic weights of elements with a reasonable degree of accuracy, although a very high degree of exactness is not essential so long as the equivalent weight be known very exactly. Two such methods have already been described, viz.,

- (a) from vapour density measurements;
- (b) from Dulong and Petit's Rule.

Others which must now be referred to briefly are:

- (c) from isomorphism;
- (d) from the Periodic System (Chapter 9).

#### *Isomorphism and Atomic Weights*

E. Mitscherlich in 1818 found that analogously constituted substances (that is substances having analogous formulae—Chapter 8) often crystallize in the same crystalline form. (Cf. Chapter 13, pages 192–196.) This he expressed in the Law of Isomorphism (sometimes called Mitscherlich's Law), viz., "*the same number of atoms combined in the same manner produce the same crystalline form.*"

This law of isomorphism can be used as a control in deducing the chemical composition of a salt; and also in atomic weight determinations for deciding between two numbers which are multiples of a common factor. The method is restricted to crystalline compounds; and it is only applicable in conjunction with other methods of atomic weight determinations since that of at least one member of the isomorphous series must be known.

Thus Mitscherlich deduced the number 79 for the atomic weight of selenium by this method, and he also gave selenious and selenic acids formulae corresponding with sulphurous and sulphuric acids respectively, on account of the isomorphism of the sulphates and the selenates. The analyses of potassium sulphate and of potassium selenate gave:

	Potassium	Oxygen	Sulphur	Selenium	Total
Potassium sulphate .	44.83	36.78	18.39	—	100.00
Potassium selenate .	44.83	36.78	—	45.40	127.01

Assuming that the molecule of potassium sulphate contains one atom of sulphur; that the molecule of potassium selenate contains the same number of atoms; and that the atomic weight of sulphur found from the composition and densities of its volatile compounds is 32, we have:

$$\text{Atomic weight S : Atomic weight Se} = 18.39 : 45.40$$

Hence,

$$\begin{aligned} 32 : \text{Atomic weight Se} &= 18.39 : 45.40 \\ \therefore \text{Atomic weight of selenium} &= 79.00 \end{aligned}$$

### *Atomic Weights and the Periodic System*

In a later chapter (Chapter 9), in which the classification of the elements is discussed, we shall see that the first satisfactory system was that due to Mendeléeff, and was based on the arrangement of the elements in the order of their atomic weights. Although modern developments have shown (cf. Chapters 9 and 10) that the atomic weight itself, along with Mendeléeff's Periodic System, depends upon something still more fundamental, nevertheless the atomic weight is approximately proportional to this more fundamental property of the atom, viz., the atomic number (see page 136). Accordingly, granted that the atomic weights of a sufficient number of elements are known to construct the table, we can use it to discover the correct value by which to multiply the equivalent weight in order to arrive at the atomic weight.

A good example is again furnished by the case of indium. According to C. L. Winkler, indium has the equivalent weight 37.8. The correct atomic weight must be some multiple of this, and for no special reason the atomic weight was once taken to be  $37.8 \times 2 = 75.6$ . In that case indium would fall in a position in the periodic table where it would be quite mis-matched. Mendeléeff proposed to consider indium as trivalent, like aluminium, so that the atomic weight would be  $37.8 \times 3 = 113.4$ , and the element would fall in the table into a place where it fits very well. The subsequent determination of the specific heat of indium 0.0577 corroborates, as we have seen, the correction made by Mendeléeff in the atomic weight from 75.6 to 113.4. The accepted value now is 114.82.

### § 6 The Atomic Weights of the Inert Gases

The determination of the atomic weights of the inert gases (see Chapter 26) presents a problem which cannot be entirely solved by any of the methods so far described in this chapter, for, as their name implies, there is no evidence that they form chemical compounds, in the ordinary sense of the word, and hence no equivalent weight can be determined, for this latter quantity is essentially a *reacting* weight.

The densities of these gases have been determined with a high degree of accuracy by various workers (e.g., Rayleigh, Ramsay, Whytlaw Gray and others), but being elementary gases, it is necessary to know also their *atomicity* (i.e., the number of atoms in a molecule of the gas) in order that their atomic weights may be calculated from their densities, which will be, as we have seen, equal to one-half of their molecular weights. Whence it follows that, if the inert gases are monatomic, their densities (relative to hydrogen) will be one-half of their atomic weights; if diatomic, the densities will be equal to the atomic weights, and so on.

The problem of the atomicity of the inert gases has been tackled in the same way as confirmation was sought for the view (deduced from chemical evidence) that the hydrogen atom is diatomic, that is to say,



by determining the ratio of the two specific heats of the gases. The theoretical assumptions on which the method is based have been discussed already in Chapter 5 (page 82).

When applied to the inert gases experiments (e.g., measurements of the velocity of sound) show that  $\gamma$  for these substances is 1.66. Hence we conclude that the inert gases are monatomic, and that their atomic weights are twice their densities (relative to hydrogen). The values so obtained fit in the periodic table satisfactorily and are accordingly accepted as correct.

### § 7 Standard Atomic Weight

It has been emphasized above that the atomic weights of the elements as used by chemists are a series of numbers indicating the *relative* weights of the atoms of the different elements. For practical purposes, therefore, it is necessary to fix a standard for atomic weights, and this standard is now universally taken to be **oxygen = 16**.

This has not always been the case, however, for during the latter part of the nineteenth century, J. Dalton's (1803) standard, hydrogen = 1, was used for the atomic weights instead of oxygen = 16. Hydrogen was selected because it is the lightest element known. J. S. Stas (1860-5) pointed out that the determination of the atomic weight of an element should be connected with the standard as directly as possible. Very few compounds of the metals with hydrogen are suitable for an atomic weight determination, while nearly all the elements form stable compounds with oxygen. Hence, if hydrogen be the standard, it is necessary to find the exact relation between the given element and oxygen, and then calculate what that relation would be on the assumption that the relation between hydrogen and oxygen is known. Every improved determination of the relation between hydrogen and oxygen would then be followed by an alteration in the atomic weight of every other element whose value, with respect to hydrogen as a standard, has been determined by the indirect process just indicated. The determination of the exact relation between hydrogen and oxygen appears to be more difficult than many other determinations, and hence the majority of chemists think it better to refer the atomic weights of the elements to oxygen = 16 as the standard instead of making the atomic weights depend on the more or less uncertain relation H : O. The standard oxygen = 16 is quite arbitrary. T. Thomson (1825) used oxygen = 1; W. H. Wollaston (1814), 10; J. S. Stas (1860-5), 16; and J. J. Berzelius (1830) used oxygen = 100 as standard. The latter number makes the atomic weights of many elements inconveniently large, and if the atomic weight of oxygen be any whole number less than 16, fractional atomic weights will be required. The use of the "oxygen-16" unit involves the least change in the numbers which were in vogue when "hydrogen-unity" was the standard.

### § 8 Accurate Atomic Weight Work

The determination of atomic weights with the highest possible degree of accuracy requires an experimental technique of a very high order and so it is that there are only one or two men in each generation whose work in this field is of such a calibre that their results command universal acceptance.

Among such men the names of J. S. Stas (1813–91), T. W. Richards (1868–1928) and O. Hönigschmid stand out as those of chemists whose work was thus accepted.

The determination of the equivalent weights and hence of the atomic weights of a limited number of elements with the greatest possible accuracy was Stas's life work, and for a great many years his results were accepted as the most accurate values. He it was who proposed oxygen as standard since, as he affirmed, the hydrogen : oxygen ratio was not known with complete certainty.

To this work Stas brought a degree of patience and skill hitherto unexampled, and he applied refinements in the methods to be used such as had never previously been attempted. He made careful search for well-defined reactions and studied minutely the conditions necessary for them to be complete; he prepared and purified all his materials with meticulous care; the balances employed were specially constructed and of the highest order of accuracy and sensitiveness available at the time; and the practical details of manipulation were worked out with the greatest pains and ingenuity.

Although Stas's work on atomic weights was the most accurate that had then been performed, it only covered a limited range of elements, and he himself expressly disclaimed any finality for his results. It was, therefore, natural that in due time this type of work should be taken up by another—and to T. W. Richards of Harvard it fell to continue and even to improve upon Stas's work.

Richards began with the intention of building upon the foundation laid by Stas in the sense of utilizing Stas's values, in particular his value for silver, and applying them to the determination of the atomic weights of other elements not investigated by Stas. But his work soon revealed the existence of small but real discrepancies which at length he was reluctantly forced to conclude were caused by systematic errors in Stas's work.

Stas had developed the use of silver as the basis for his work. The element under examination was converted into its chloride, or bromide, which was then used, with silver nitrate solution, to precipitate silver chloride, or bromide. The results so obtained had been related to oxygen by Stas as follows. He began by heating potassium chlorate and determining the loss of weight consequent upon the driving off of the oxygen (known to be six equivalents). The potassium chloride was then precipitated with silver nitrate, the value for silver itself being determined by burning pure silver in a current of chlorine.

Richards, in his earlier work, made use of Stas's values for silver and chlorine so obtained, but when discrepancies began to reveal themselves he was led to a critical examination of Stas's work, and thus to the discovery of the systematic errors in it.

The principal sources of these errors were found to be:

- (i) even the most carefully purified potassium chlorate always contains chloride;
- (ii) silver chloride when precipitated by potassium chloride tends to carry down traces of the latter which cannot be removed by washing;
- (iii) Stas had at times carried out precipitation using *solid* chloride, thus aggravating the error of (ii);

(iv) Stas had worked with abnormally large quantities which had rendered the adequate washing of precipitates difficult;

(v) there were slight inaccuracies in the end points of Stas's analyses owing to the slight solubilities of silver halides and the effect of excess of one or other of the reagents on these solubilities;

(vi) Stas's silver had contained oxygen.

As a consequence Richards undertook the revision of these fundamental atomic weights of silver, chlorine and nitrogen.

### § 9 Richards's Determination of the Atomic Weights of Silver, Chlorine and Nitrogen

Richards and his co-workers attacked the problem of the atomic weights of silver, nitrogen and chlorine in the following way. They determined (i) the weight of silver in a given weight of silver chloride; (ii) the weight of silver chloride obtained from a given weight of ammonium chloride; and (iii) the weight of silver nitrate formed from a given weight of silver. From the results of these experiments, taking oxygen as 16.000 and using Morley's value (see below—§ 11) for hydrogen (1.0076), the atomic weights of silver, nitrogen and chlorine can be calculated in terms of those of oxygen and hydrogen, independently of each other, or of any other determinations.

For this work pure silver was obtained by the reduction of silver nitrate, which had been fifteen times recrystallized, the silver being fused on lime in an atmosphere of hydrogen. The silver was dissolved in the purest nitric acid, the resulting solution diluted and silver chloride precipitated from it by a solution of very pure common salt. The determination was carried out in a red light and the end point of the reaction was accurately found by the use of the *nephelometer* (see below) specially developed by Richards for the purpose. The precipitate was filtered off, washed, dried and weighed with every possible precaution.

Two methods were employed for the preparation of pure ammonium chloride. In one ammonium sulphate, treated with an acid solution of potassium permanganate to oxidize away all organic matter, was made to yield ammonia by treatment with pure lime, and the resulting gas was absorbed in the purest hydrochloric acid. The solution was evaporated and the ammonium chloride sublimed. In the other method the ammonium sulphate used as a source of ammonia was obtained by the electrolytic reduction of pure nitric acid.

Ammonium chloride so prepared was weighed out with every possible precaution, dissolved in very pure distilled water and added to a solution of silver nitrate prepared as described above. The resulting precipitate was treated and weighed in an exactly similar manner.

Very pure silver nitrate was prepared by dissolving a weighed quantity of the purest silver, obtained as already described, in nitric acid repeatedly redistilled and diluted with very pure water. The experiment was carried out in a quartz flask and the solution was evaporated to dryness in a gentle current of air. The resulting silver nitrate was dried and weighed with great care and accuracy.

As a result of these three series of experiments the ratios of silver chloride to silver, ammonium chloride to silver chloride, and silver nitrate to silver were found with very great accuracy. These results connect the atomic weight of nitrogen with those of silver, chlorine and hydrogen.

Representative results obtained by Richards are:

1.00000 gm. of silver gave 1.32867 gm. of silver chloride.

1.00000 gm. of silver chloride was precipitated by 0.373217 gm. of ammonium chloride.

1.00000 gm. of silver yielded 1.57497 gm. of silver nitrate.

The calculation of the atomic weights is then as follows:

Let the atomic weight of silver =  $x$   
 Let the atomic weight of chlorine =  $y$   
 Let the atomic weight of nitrogen =  $z$



a consideration of the superior suitability of certain precipitates by reason of the greater ease with which occluded impurities could be removed. Thus, in addition to the use of solutions of as high a dilution as practicable, a precipitate which has a sponge-like structure is better than a rigid crystalline one, since the innermost pores of a spongy precipitate are accessible, whereas those of a crystalline one are not. Hence, thorough washing is more likely to prove effective in the former case. It is fortunate that silver chloride is a precipitate of a spongy character.

Richards also developed the use of the centrifuge for the separation of solids from their mother liquor, a process which finds wide application in technical processes, but which had not been used by scientific investigators to anything like the same extent. There is little doubt that the extensive use of this process has contributed much to the success of Richards and his co-workers in this field.

Another improvement in technique due to Richards is the bottling apparatus: a device whereby substances can be heated for drying purposes, in any desired gas, or in a vacuum, under exactly reproducible conditions, and then weighed without exposure to the air at any stage.

The bottling apparatus is shown diagrammatically in Fig. 7.1.

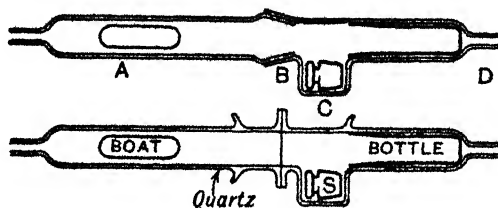


FIG. 7.1.—Richards's Bottling Apparatus

(By permission of the Chemical Society)

It consists of a wide glass tube of quartz glass *A* fitted by means of a ground joint to a similar tube of soft glass which has a projection or pocket *C* in one side. The boat containing the substance to be dried is heated in the hard glass tube surrounded by an atmosphere of any desired gas, or gases. The weighing bottle is placed in the other end of the apparatus. After cooling these gases are displaced by pure dry air and the boat transferred to the weighing bottle by slightly tilting the apparatus, after which the stopper *S* is similarly inserted. The weighing bottle can then be transferred to a balance for weighing by opening the apparatus at the joint.

Another point to which Richards directed careful attention was the slight solubility of all so-called "insoluble" substances. Glass is not entirely unaffected by water, and in consequence the precipitates obtained by some previous workers were probably contaminated by traces of silica. Richards avoided this difficulty by the use, where possible, of platinum vessels; otherwise quartz was used. Further, when the determination depends upon the precipitation of such a substance as silver chloride, which is ultimately weighed, its small but perceptible solubility in water must be allowed for, both in connection with the original precipitation and also in the subsequent washing of the precipitate. (Cf. page 262—solubility product.)

This problem was solved by Richards by means of a device which he called a nephelometer (= cloud-measurer). The construction of this apparatus is very simple. It consists of two test tubes *f* near together and slightly inclined to one another, arranged near a bright light from which they can be shaded, either wholly or partially, by means of sliding shades *g*. The tubes are observed from above by means of two prisms *d* of very small angle so that they can be observed simultaneously and their brightness accurately compared. The arrangement is indicated by Fig. 7.2.

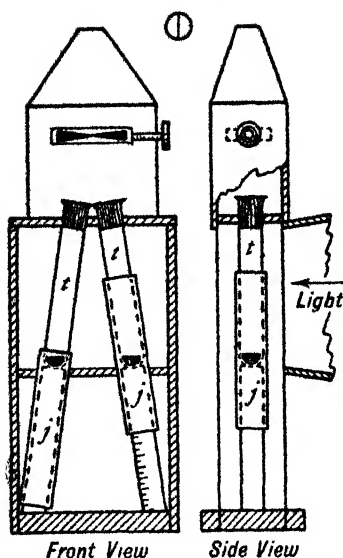


FIG. 7.2.—The Nephelometer

In estimating the amount of silver chloride carried away in the wash water for example, the washings are treated with excess of a solution of silver nitrate which causes the precipitation of a small quantity of silver chloride (due to the common-ion effect, see Chapter 18, page 262), so that the solution becomes faintly opalescent. This is done in one of the tubes of the nephelometer while a solution of a known amount is treated similarly in the other tube. Each precipitate reflects light so that the tubes appear faintly luminous. The shades are adjusted until the tubes appear to be equally bright. By comparing the lengths of the tubes then exposed to the light, the amount of precipitate in the "unknown" solution can be calculated.

Other precautions referred to by Richards may also be mentioned. Traces of solids are easily lost when solutions are evaporated to dryness, and to avoid this, very carefully controlled conditions must be employed and the results checked by blank experiments. All substances must be rigorously protected from dust by the use of suitable hoods and closed vessels. Heating by coal-gas tends to cause contamination by impurities from the gas, this is avoided by the use of electrical heating.

To sum up we may quote Richards's own words:

"Every substance must be assumed to be impure, every reaction must be assumed to be incomplete, every method of measurement must be assumed to contain some constant error, until proof to the contrary can be obtained. As little as possible must be taken for granted."

## § 11 The Ratio of the Weights of Hydrogen and Oxygen in Water

The calculation of the atomic weights of silver, nitrogen and chlorine given in § 9 illustrates the fact that in this method at least the final result depends upon a knowledge of the atomic weight of hydrogen in terms of that of oxygen. This serves to illustrate the fundamental importance of this latter ratio, and an account of some representative determinations of it must now be given.

Two distinct methods are available: either the weight of hydrogen combining with a given weight of oxygen can be found, or the ratio in which these gases combine by volume can be determined, whence, from a knowledge of their densities, the ratio in which they combine by weight can be calculated.

The most accurate determinations of the oxygen : hydrogen ratio are those made by Morley (1895), who measured the ratio by weight, and by Burt and Edgar (1915), who measured the ratio by volume.

*Morley's Determination of the Composition of Water by Weight*

Historically, the most important measurement of the composition of water by weight had been made in 1842 by Dumas. He had synthesized water by passing purified hydrogen over red-hot copper oxide and collecting the water so formed. Since the quantities are interdependent, he measured the weight of oxygen used and the weight of water formed, obtaining by difference the weight of hydrogen concerned. He was thus able to avoid the very difficult operation of weighing the hydrogen directly. (Cf. Chapter 20, page 302.)

A notable feature of Morley's investigation was the fact that he weighed both the hydrogen and the oxygen used, *and* the water formed, whereas previous investigators had determined one of these quantities by difference. The accuracy of his work is indicated by the very close agreement among themselves of the values he found for these three quantities.

Morley prepared the oxygen used from potassium chlorate and purified it by passing it through a series of three wide tubes. The first contained glass beads moistened with strong potassium hydroxide solution; the second, beads similarly moistened with sulphuric acid; and the third, phosphorus pentoxide and glass wool. After purification the gas was collected in large glass globes, previously evacuated.

Hydrogen was obtained by the electrolysis of dilute sulphuric acid, and purified by being passed successively through strong potassium hydroxide solution, over red-hot copper and then through three long drying tubes similar to those employed for the oxygen. There is always a difficulty in weighing hydrogen accurately on account of its very low density, which means that very small errors in the weighing of the containing vessel are magnified some 500 times relative to the weight of hydrogen deduced. Morley obviated this difficulty by absorbing his hydrogen in metallic palladium. Palladium is a metal (see page 292) which possesses the property of absorbing some 800 times its own volume of hydrogen gas, and of giving up the gas again when heated to a dull red heat. By this means the magnification of errors in the weight of hydrogen can be avoided.

Both the globe containing the oxygen and the palladium tube containing the hydrogen were weighed with every possible precaution. (Cf. Chapter 3, page 29.)

The globe containing oxygen was connected with *C*, Fig. 7.3. The oxygen passed through a layer of phosphorus pentoxide,\* and thence into the glass chamber *M* via one of the jets *A*; the tube containing hydrogen was similarly connected with another tube, *D*, containing phosphorus pentoxide, and the hydrogen led into the chamber *M* via one of the jets *A*. The rates at which the gases enter the chamber were regulated by suitable stopcocks. The chamber *M* was previously

\* The phosphorus pentoxide is not intended to dry the gases (they have already been dried) but to prevent loss of water at the later stage.

evacuated and weighed. One of the gases, say oxygen, was allowed to enter *M*, and electric sparks were passed across the terminals *F* just

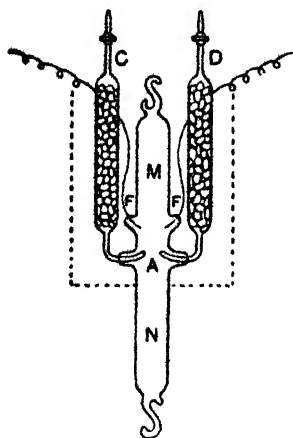


FIG. 7.3.—Morley's Experiment Synthesis of Water

over the jets *A*. Hydrogen was led into the apparatus and ignited by the sparks. The rates at which hydrogen and oxygen entered the chamber were regulated so that the formation of water was continuous. The water formed was condensed, and collected in the lower part of the chamber. To hasten the condensation, the apparatus was placed in a vessel of cold water—dotted in the diagram. When a sufficient amount of water was formed, the apparatus was placed in a freezing mixture. The mixture of unconsumed oxygen and hydrogen remaining in the tube was pumped away, and analysed. The weights of hydrogen and oxygen so obtained were added to the weights of unconsumed hydrogen and oxygen remaining in the globes. The phosphorus pentoxide tubes prevented the escape of water vapour. The amounts

of hydrogen and oxygen used were determined from the weights of the vessels containing them before and after the experiment. The amount of water formed was determined from the increase in the weight of the above-described vessel after the combustion. Morley, as a mean of eleven experiments, found that:

Hydrogen used	.	.	.	.	3.7198 grams
Oxygen used	.	.	.	.	29.5335 grams
Water formed	.	.	.	.	33.2530 grams

Hence, taking oxygen = 16 as the unit for combining weight, it follows that 16 *parts by weight of oxygen combine with 2.0152 parts by weight of hydrogen to form 18.0152 parts of water*—within the limits of the small experimental error.

#### *Burt and Edgar's Determination of the Composition of Water by Volume*

Some account of Burt and Edgar's work on the volume composition of water has been given in Chapter 5 (page 74). As a result of fifty-nine determinations, they found the ratio 1 : 2.00288 for the combining volumes of oxygen and hydrogen in water. In conjunction with accurate values for the absolute densities of oxygen and hydrogen this result enables us to calculate a value for the ratio in which oxygen and hydrogen combine by weight. Morley (who determined this ratio by weight *directly*, with great accuracy, as described above) also made very careful measurements of the absolute densities of hydrogen and oxygen. His values are that the weights of one litre of hydrogen and



oxygen at S.T.P. are 0.089873 gm. and 1.42900 gm. respectively. In conjunction with Burt and Edgar's value for the volume ratio, we then find the ratio for the atomic weights of oxygen and hydrogen to be 16 : 1.0077.

## § 12 Atomic Weight Determinations by Physical Methods

We have already seen (this chapter, § 6) that the atomic weights of the inert gases can only be determined by the application of physical principles, since they form no compounds and hence have no equivalent (or reacting weight). It is natural that for other elements confirmation of the chemical values should be sought from the results of purely physical measurements. An account of some representative work in this field must, therefore, now be given.

Until recently, the most important of these methods was the so-called "limiting density" method. The great problem confronting attempts to determine atomic weights from values of gas densities arises from the fact that all gases show deviations from the gas laws in greater or less degree, and that the extent of these deviations varies from gas to gas. For this reason the ratio of the normal densities of two gases (as defined in Chapter 3, page 28) will not give the *exact* ratio of their molecular weights. For, if equal volumes of two given gases, measured at one particular pressure, did actually contain *exactly* the same number of molecules as required by Avogadro's hypothesis, it follows that at some other pressure, owing to the different compressibilities of the two gases, equal volumes would contain slightly different (although nearly the same) number of molecules.

It has been found that differences between various gases as regards their deviations from Boyle's Law, as well as the extent of the deviations, become very much smaller as the pressure is reduced, and hence it is reasonable to assume that at zero pressure these differences would vanish, and that the ratio of the densities of two gases at zero pressure (known as the *limiting densities*) would be an *accurate* value for the ratio of the molecular weights of the gases concerned.

The limiting density of a gas cannot be determined directly, but it can be evaluated from the density at S.T.P. if certain other factors can be found.

Suppose that a quantity of gas of mass  $m$  gm. occupies a volume of  $v$  litres at a temperature of  $0^\circ \text{C}$  and a pressure of  $p$  atmospheres. If Boyle's Law were obeyed, the quantity  $m/pv$  would be the same at all pressures. Owing to deviations from Boyle's Law, it will, in fact, vary with the pressure. If  $p = 1$ , its value is that of the normal density as defined in Chapter 3. As  $p$  approaches zero, its value approaches that of the limiting density. Now for any given gas, whose normal density (i.e., at S.T.P.) is  $D$ ,

$$D = \frac{m}{p_1 v_1}$$

where  $p_1 v_1$  is the value of  $p v$  when  $p = 1$ . Similarly, the limiting density is  $\frac{m}{p_0 v_0}$  where  $p_0 v_0$  is the limiting value of  $p v$  as  $p$  approaches zero.

$$\therefore \text{Limiting density} = D \times \frac{p_1 v_1}{p_0 v_0}$$

The evaluation of the limiting density is thus a matter of determining the ratio  $p_1 v_1 / p_0 v_0$ . This ratio, for any given mass of gas, can be found by either of two distinct methods. These are:

- (i) the extrapolation method;
- (ii) on the assumption that the deviation from Boyle's Law is proportional to the pressure, the measurement of  $p v$  at two low pressures enables  $p_0 v_0$  to be calculated. This is known as the **compressibility coefficient method**.

**The extrapolation method**

By making a number of determinations of  $p_v$  at various pressures, a curve can be plotted which expresses the relation between  $p_v$  and  $p$ . This curve can then be extrapolated back to  $p = 0$ , which enables the value of  $p_0 v_0$  to be found, and hence the ratio  $p_1 v_1 / p_0 v_0$ .

**The compressibility coefficient method**

If the deviation of a gas from Boyle's Law is proportional to the pressure, we can then say the relative deviation,

$$\frac{p_0 v_0 - p v}{p v} = \lambda p,$$

where  $\lambda$  is a constant called the **compressibility coefficient**. Two measurements of  $p v$  for different values of  $p$  (less than one atmosphere) will serve for the calculation of  $\lambda$  from this expression. Having found  $\lambda$  we see that

$$p_0 v_0 = p_1 v_1 (1 + \lambda) \text{ since } p = 1;$$

$$\text{whence Limiting density} = \frac{\text{Normal density}}{1 + \lambda}$$

For example, the following values have been obtained for oxygen and hydrogen:

	Normal Density	Compressibility
Oxygen . . . .	1.42900	+ 0.000964
Hydrogen . . . .	0.089873	- 0.00054

$$\therefore \text{Limiting density of oxygen} = \frac{1.4290}{1.000964} = 1.42762 \text{ gm./litre.}$$

$$\text{and Limiting density of hydrogen} = \frac{0.089873}{0.99946} = 0.089922 \text{ gm./litre.}$$

Since these are in the ratio of the molecular weights, and hence, being diatomic molecules, of the atomic weights, it follows that the hydrogen : oxygen ratio measured in this way is

$$16 : 1.0078$$

This value compares very well with those obtained by Morley (page 110) and Burt and Edgar (page 111).

Examples of the use of the limiting density method for finding atomic weights are Moles and Batuecas's value for nitrogen, obtained from the limiting density of ammonia; and Gray and Burt's value for chlorine, from that of hydrogen chloride.

As a result of their experiments with ammonia, Moles and Batuecas found the limiting density of ammonia to be 0.75990 gm. per litre. The limiting density of oxygen (determined similarly by Gray and Burt) is 1.42762 gm. per litre. The density of ammonia, referred to oxygen 16, is thus:

$$\frac{0.75990}{1.42762} \times 16 = 8.516$$

Its molecular weight is therefore 17.032, which gives the value 14.0086 for the atomic weight of nitrogen, on the basis of hydrogen 1.0078.

In Gray and Burt's experiments with hydrogen chloride the following figures were obtained:

$$\text{Normal density} = 1.63915 \text{ gm. per litre}$$

$$p_1 v_1 = 54803$$

$$\text{By extrapolation } p_0 v_0 = 55213$$

$$\therefore \text{Limiting density of hydrogen chloride}$$

$$= \frac{1.63915 \times 54803}{55213}$$

$$= 1.62698 \text{ gm. per litre.}$$

As above, the limiting density of oxygen is 1.42762 gm. per litre,  $\therefore$  Density of hydrogen chloride, referred to oxygen 16,

$$\begin{aligned} &= \frac{1.62698}{1.42762} \times 16 \\ &= 18.233. \end{aligned}$$

The molecular weight of hydrogen chloride, therefore, is 36.466, which gives 35.458 as the value of the atomic weight of chlorine.

Values such as these are in excellent agreement with those found by chemical methods. It is therefore concluded that the limiting density method is capable of a degree of accuracy equal to that of the best chemical determinations.

During recent years, Aston has measured the atomic weights of many elements by means of the perfected forms of the mass-spectrograph, and a very high degree of accuracy has been attained. The description of this method of atomic weight determination must, however, be deferred until the far-reaching modern discoveries concerning the nature of matter have been described, for the theory of the method depends upon these modern results. An account will accordingly be found at the end of Chapter 10.

### § 13 International Atomic Weights

However great the care and ingenuity which may be expended in perfecting the methods to be used, and in eliminating errors from determinations of such quantities as atomic weights, it nevertheless remains true that all such measurements are affected by unavoidable errors of experiment, which, even though extremely small, are yet real. Hence it is that even the best available determinations of such a quantity as the atomic weight of an element differ among themselves within narrow limits.

This being the case, it is convenient, for practical purposes, to select one representative value from the many different observations ranging between these limits. The majority of chemists have agreed to accept the Report of the Commission on Atomic Weights to the Conference of the International Union of Pure and Applied Chemistry year by year as determining what are the best representative values for the atomic weights of all the elements. Every time new and more refined methods of measurement are employed, a change—generally insignificantly small—may be necessary.

A careful consideration of all the available evidence considerably reduces the risk of error, and this method, adopted by the Commission, appears to be the most satisfactory solution of the problem.

The atomic weights of a few of the more important elements are indicated in Table VI. The numbers are those recommended by the Commission on Atomic Weights. The full table appears inside the front cover of this book.

For ordinary calculations involving the use of atomic weights, all the atomic weights, excepting chlorine (35.5), copper (63.5), nickel (58.5),

and zinc (65.5), are rounded off to the nearest whole numbers. The elements just named are then assigned the atomic weights indicated in the brackets. Some chemists—G. D. Hinrichs, for example—have believed that the rounded numbers are the best representative values of the atomic weights, and that the small deviations from the rounded numbers indicated in the "International Table" represent

TABLE VI.—INTERNATIONAL ATOMIC WEIGHTS. 0 = 16

Aluminium . . . . .	Al	26.98	Iron . . . . .	Fe	55.85
Antimony . . . . .	Sb	121.76	Lead . . . . .	Pb	207.21
Arsenic . . . . .	As	74.91	Magnesium . . . . .	Mg	24.32
Barium . . . . .	Ba	137.36	Manganese . . . . .	Mn	54.94
Bismuth . . . . .	Bi	209.0	Mercury . . . . .	Hg	200.61
Boron . . . . .	B	10.82	Nickel . . . . .	Ni	58.71
Bromine . . . . .	Br	79.916	Nitrogen . . . . .	N	14.008
Calcium . . . . .	Ca	40.08	<b>Oxygen</b> . . . . .	<b>O</b>	<b>16.00</b>
Carbon . . . . .	C	12.011	Phosphorus . . . . .	P	30.975
Chlorine . . . . .	Cl	35.457	Platinum . . . . .	Pt	195.09
Chromium . . . . .	Cr	52.01	Potassium . . . . .	K	39.10
Cobalt . . . . .	Co	58.94	Silicon . . . . .	Si	28.09
Copper . . . . .	Cu	63.54	Silver . . . . .	Ag	107.88
Fluorine . . . . .	F	19.0	Sodium . . . . .	Na	22.991
Gold . . . . .	Au	197.0	Sulphur . . . . .	S	32.066
Hydrogen . . . . .	H	1.008	Tin . . . . .	Sn	118.7
Iodine . . . . .	I	126.91	Zinc . . . . .	Zn	65.38

real, if unrecognized, errors of experiment. In view of the work on **isotopes**, to be discussed in a later chapter, this question has lost its significance until we have learned to interpret the fact that many of the atomic weights at present accepted are averages of mixtures of two or more different kinds of atoms which at present are given the same name, although they have slightly different atomic weights. So far as has yet been observed, these atoms cannot be distinguished from one another by any chemical process yet tried.

## CHAPTER 8

# FORMULAE AND EQUATIONS

However certain the facts of any science, however just the ideas derived from these facts, we can only communicate false or imperfect impressions to others, if we want words by which these may be properly expressed.—A. L. LAVOISIER.

In his calculations the chemist relies on the supposed chemical relations of the invisible, intangible, and immeasurable particles he calls atoms. These relations have been determined by others in whom he has confidence, and the accuracy of these constants has to be accepted on faith.—H. C. BOLTON.

### § 1 Symbols and Formulae

FOR convenience in recording and working on the facts of chemistry in so far as they concern the composition of substances, there has been developed a system of symbols and nomenclature, based upon the Atomic Theory (see Chapter 4, page 70). To each element has been assigned a **symbol** consisting of one or two letters derived from the recognized name of the element (in some cases the Latin name, e.g., Hg for mercury from the Latin *hydrargyrum*). Compounds are similarly represented by joining together the symbols for the different elements present in the compound, with appropriate subscript numerals to indicate the number of atoms of each element present in one molecule of the compound. Familiar examples are  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  representing water and sulphuric acid respectively. Such a juxtaposition of symbols, representing a compound, is called a **formula**—the formula of the compound.

It is important to notice that these symbols and formulae do not merely represent the elements and their compounds in a qualitative or purely descriptive manner, but are quantitative. Thus the symbol of an element represents a definite *weight* of that element, numerically equal to the atomic weight, expressed in a convenient unit (e.g., grams or pounds). Similarly, the formula of a compound expresses a definite *weight* of the substance, being in fact the numerical sum of the atomic weights of the constituent atoms expressed in suitable units as before.

### § 2 Equations

The elements are represented by *symbols*, and compounds are indicated by combinations of symbols called *formulae*: the chemical changes which take place when elements or compounds react are similarly shown by means of **equations**.

When the initial and final products of a chemical reaction as well as the composition and proportions of the molecules concerned in the

reaction are known, the facts can usually be symbolized in the form of a chemical equation.

Such an equation indicates the nature of the atoms and the supposed composition of the molecules concerned in the reaction; as well as the proportions of the different molecules in the initial and final products of the reaction. For instance, when mercury is heated in air, and mercuric oxide,  $\text{HgO}$ , is formed, the reaction can be represented in symbols:  $2\text{Hg} + \text{O}_2 = 2\text{HgO}$ . We here ignore the nitrogen of the air because, so far as we can tell, it plays no direct part in the chemical reaction. Similarly, when mercuric oxide is heated to a high temperature it decomposes, forming metallic mercury and oxygen. In symbols,  $2\text{HgO} = 2\text{Hg} + \text{O}_2$ . The symbol " $=$ " is used instead of the words "produces" or "forms," and the symbol " $+$ " is used for "together with" on the right side of the " $=$ " sign, and for "reacts with" on the left side. The latter equation reads: "Two molecules of mercuric oxide, on decomposing, produce a molecule of oxygen and two molecules of monatomic mercury." The number and kind of the atoms of the two sides of the equation must always be the same (Law of Conservation of Matter).

In Chapter 5 (page 77) we saw that the molecular weight of an element or compound is the sum of the atomic weights of all the atoms contained within a molecule of that particular element or compound; and as mentioned above, all symbols and formulae have a quantitative significance. Hence it follows that an equation indicates the proportions by weight of the substances concerned in the reaction. The atomic weight of mercury is 200, and the atomic weight of oxygen is 16, hence, the molecular weight of mercuric oxide is 216, and of oxygen 32. The latter equation can therefore be read: "432 grams (oz. or tons) of mercuric oxide, on decomposing, forms 32 grams (oz. or tons) of oxygen gas and 400 grams (oz. or tons) of metallic mercury." Thus, the chemical equation can be employed in all kinds of arithmetical problems dealing with weights of substances formed or produced.

Further (Chapter 5, page 85), the molecular weight in grams of any gas will occupy 22.4 litres at S.T.P. It follows, therefore, that **an equation indicates the proportion by volume of the gases concerned in the reaction**. Consequently, we can express the idea conveyed by the equation  $2\text{HgO} = \text{O}_2 + 2\text{Hg}$  in these words: "432 grams of mercuric oxide will furnish 32 grams of oxygen, or 22.4 litres of oxygen gas at  $0^\circ \text{C}$ . and 760 mm., and 400 grams of mercury."

### § 3 Deduction of Formulae

#### 1. From percentage composition

The formula of a compound, expressing the number and kind of atoms present in its molecule, is usually found from the results of experiment—the following four sets of data being required:

- (i) information as to the elements present in the compound;
- (ii) the percentage composition of the compound;
- (iii) the atomic weights of the elements present;
- (iv) the molecular weight of the compound.

(i) *The elements present.* The nature of the elements present is found by the processes of *qualitative* analysis, and as a rule no great difficulty is experienced in obtaining these necessary data.

(ii) *The percentage composition.* The percentage composition, or proportion by weight of each element present, is found by means of a *quantitative* analysis. The elements in a known weight of the compound are converted into some form in which they can be separated and weighed. Examples of this type of investigation have already been given in Chapters 6 and 7, and many others will be found in later chapters.

(iii) *The atomic weights,* found as described in Chapter 7, are derived, for purposes such as that now under consideration, from tables such as that printed on the inside of the front cover of this volume.

(iv) *The molecular weight* of the compound is discovered either by means of one of the methods described previously (Chapter 5) or by one of those referred to in Chapter 14.

The application of these data to the discovery of an actual formula is best explained by means of an example.

*A volatile compound containing carbon and hydrogen only was found to have the following percentage composition: Carbon, 92.31 per cent, Hydrogen, 7.69 per cent. The density of the vapour of the substance (referred to hydrogen) was 39. Calculate its formula.*

From the table on the inside of the front cover, we find that the atomic weights of carbon and hydrogen are approximately 12 and 1 respectively. In order to find the relative numbers of atoms of carbon and of hydrogen in the weights of these elements given in the percentage composition, we must divide these weights by the respective atomic weights.\* We thus arrive at the following result:

Number of carbon atoms : number of hydrogen atoms

$$= \frac{92.31}{12} : \frac{7.69}{1}$$

$$= 7.69 : 7.69.$$

\* Let the formula be  $A_xB_yC_z$ , and let the atomic weights of  $A$ ,  $B$  and  $C$  be  $a$ ,  $b$  and  $c$  respectively. Then

$$\begin{aligned} \text{percentage of } A &= \frac{100 ax}{ax + by + cz}, \text{ i.e., } \frac{\text{percentage of } A}{a} = \frac{100 x}{ax + by + cz} \\ \text{percentage of } B &= \frac{100 by}{ax + by + cz}, \text{ i.e., } \frac{\text{percentage of } B}{b} = \frac{100 y}{ax + by + cz} \\ \text{and percentage of } C &= \frac{100 cz}{ax + by + cz}, \text{ i.e., } \frac{\text{percentage of } C}{c} = \frac{100 z}{ax + by + cz} \\ \therefore x : y : z &= \frac{\text{percentage of } A}{a} : \frac{\text{percentage of } B}{b} : \frac{\text{percentage of } C}{c} \end{aligned}$$

By the atomic theory we cannot have fractions of atoms, hence dividing by 7.69 we have the ratio 1 : 1 which leads to the formula CH. But compounds  $C_2H_2$ ,  $C_3H_3$ ,  $C_nH_n$  would clearly lead to the same result.

In the case under consideration, since the vapour density of the compound is 39, its molecular weight is 78. The molecular weight of  $C_nH_n$  is  $13n$  whence  $n = 6$ . The formula of the compound is thus  $C_6H_6$ .

In calculating formulae for substances which cannot be vaporized, and to which one of the methods to be described later cannot be applied, it is usual to assume that the molecule has the simplest possible formula. In that case the formula is said to be *empirical*. Some prefer to use the term "formula weight" in place of "molecular weight" when the actual molecular weight has not been determined. The **formula weight**, like the molecular weight of a compound, is the sum of the atomic weights of the elements represented by the known, or assumed, formula of the compound.

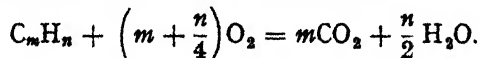
## 2. From volume relationships

When gases are involved, either among the products or starting materials of a reaction, the tedious processes required for the weighing of gases may often be avoided and the formula calculated by the application of Gay-Lussac's Law of Volumes (page 74) to the volume relationships of the reacting substances and their products.

The method can best be explained by means of an example.

*5 c.c. of a gas containing only carbon and hydrogen were mixed with an excess of oxygen (30 c.c.) and the mixture exploded by means of an electric spark. After the explosion, the volume of the mixed gases remaining was 25 c.c. On adding a concentrated solution of potassium hydroxide, the volume further diminished to 15 c.c., the residual gas being pure oxygen. All volumes have been reduced to S.T.P. Calculate the formula of the hydrocarbon gas.*

Let the formula of the gas be  $C_mH_n$ . Then the change, when it is exploded with excess oxygen, may be represented:



That is, by Gay-Lussac's Law of Volumes (page 74) and Avogadro's Hypothesis (page 76).

1 volume of hydrocarbon needs  $\left(m + \frac{n}{4}\right)$  volumes of oxygen to produce  $m$  volumes of carbon dioxide and, if the experiment be performed at room temperature, a negligible volume of condensed liquid water,

$$\therefore \text{Volume before explosion} = 1 + m + \frac{n}{4} + \text{unneeded oxygen}$$



and volume after explosion =  $m +$  unneeded oxygen

$$\therefore \text{Contraction on explosion} = 1 + \frac{n}{4}$$

The addition of potassium hydroxide removes the carbon dioxide; hence  $m$  volumes of carbon dioxide are removed in this way. Adjusting the numbers given in the example to correspond to 1 volume of hydrocarbon, we have:

Contraction on addition of potassium hydroxide

$$= m = \frac{10}{5} = 2 \quad \text{and}$$

$$\text{Contraction on explosion} = 1 + \frac{n}{4} = \frac{10}{5} = 2$$

$$\therefore n = 4$$

$\therefore$  The formula of the hydrocarbon is  $C_2H_4$ .

#### § 4 Chemical Calculations

In view of the fact that the symbols and formulae which are employed in writing the equations which represent chemical reactions have a quantitative significance, they and these equations themselves can be made the basis for many chemical calculations.

A few representative examples of these calculations follow.

1. Calculate the percentage composition of potassium nitrate  $KNO_3$ . ( $K = 39$ ,  $N = 14$ ,  $O = 16$ )

Since the formula of a compound represents the number of atoms contained in its molecule, and the atomic weights are the relative weights of these atoms, we have

one atom of potassium = 39 parts by weight  
and one atom of nitrogen = 14 parts by weight  
and three atoms of oxygen = 48 parts by weight

are combined in one molecule of potassium nitrate } = 101 parts by weight.

$\therefore$  in 100 parts by weight of potassium nitrate there are

$$\frac{39}{101} \times 100 = 38.61 \text{ parts by weight of potassium}$$

$$\frac{14}{101} \times 100 = 13.86 \text{ parts by weight of nitrogen}$$

$$\text{and } \frac{48}{101} \times 100 = 47.52 \text{ parts by weight of oxygen.}$$

That is to say, the percentage composition of potassium nitrate is:

potassium	.	.	.	38.61 per cent
nitrogen	.	.	.	13.86 per cent
oxygen	.	.	.	47.52 per cent

2. 5 gm. of zinc are completely converted into crystallized zinc sulphate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . What weight of zinc sulphate is obtained? ( $\text{Zn} = 65.5$ ,  $\text{S} = 32$ ,  $\text{O} = 16$ ,  $\text{H} = 1$ )

One atom of zinc is present in one molecule of zinc sulphate.

$\therefore$  65.5 parts by weight of zinc will yield

$$65.5 + 32 + (4 \times 16) + 7(16 + 2) = 287.5$$

parts by weight of crystallized zinc sulphate

$$\therefore 5 \text{ gm. of zinc will give } \frac{287.5 \times 5}{65.5}$$

$$= 21.95 \text{ gm. of crystallized zinc sulphate.}$$

3. What weight of iodine will be liberated by the action of the right amount of chlorine on a solution containing 2 gm. of potassium iodide, according to the equation  $2\text{KI} + \text{Cl}_2 = 2\text{KCl} + \text{I}_2$ , and what weight of chlorine will be needed? ( $\text{K} = 39$ ,  $\text{Cl} = 35.5$ ,  $\text{I} = 127$ .)

The equation shows that  $2 \times (39 + 127)$  gm. of potassium iodide are acted upon by  $2 \times 35.5$  gm. of chlorine with the formation of  $2 \times 127$  gm. of iodine.

$\therefore$  2 gm. of potassium iodide will yield

$$\frac{2 \times 127 \times 2}{2 \times (39 + 127)} = \frac{2 \times 127}{166} = 1.53 \text{ gm. of iodine.}$$

Similarly, the weight of chlorine required will be

$$\frac{2 \times 35.5 \times 2}{2 \times (39 + 127)} = \frac{2 \times 35.5}{166} = 0.43 \text{ gm. of chlorine.}$$

4. What weight of anhydrous sodium sulphate and what volume of carbon dioxide, measured at  $15^\circ \text{C}$ . and 735 mm. pressure, can be obtained by the action of excess of dilute sulphuric acid on 10 gm. of washing soda crystals,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ? ( $\text{Na} = 23$ ,  $\text{C} = 12$ ,  $\text{H} = 1$ ,  $\text{O} = 16$ ,  $\text{S} = 32$ .) The equation for the reaction (cf. Chapter 22) is



whence we see that:

286 grams of washing soda will yield 142 grams of sodium sulphate, and 22.4 litres of carbon dioxide at S.T.P.

$\therefore$  10 grams of washing soda will produce

$$\frac{142 \times 10}{286} = 4.96 \text{ grams of sodium sulphate}$$

$$\text{and } \frac{22.4 \times 10}{286} \text{ litres of carbon dioxide at N.T.P.}$$

$$= \frac{22.4 \times 10}{286} \times \frac{288}{273} \times \frac{760}{735} \text{ litres at } 15^\circ \text{C. and 735 mm}$$

$$= 0.854 \text{ litre.}$$

5. What weight of silver chloride would be precipitated if 100 c.c. of hydrogen chloride gas, measured at  $12^\circ \text{C}$ . and 750 mm. pressure, were passed into excess of a solution of silver nitrate? ( $\text{H} = 1$ ,  $\text{Cl} = 35.5$ ,  $\text{Ag} = 108$ .)

The equation for this reaction (cf. Chapter 29) is



That is to say,

22,400 c.c. of hydrogen chloride at S.T.P. will precipitate  
143.5 gm. of silver chloride.

Now 100 c.c. of hydrogen chloride at 12° C. and 750 mm.

$$= \frac{100 \times 273 \times 750}{285 \times 760} \text{ c.c. at S.T.P.}$$

Since 22,400 c.c. of hydrogen chloride at S.T.P. will precipitate 143.5 gm. of silver chloride

$$\therefore \frac{100 \times 273 \times 750}{285 \times 760} \text{ c.c. at S.T.P. will precipitate}$$

$$\frac{143.5 \times 100 \times 273 \times 750}{285 \times 760 \times 22,400} \text{ gm. of silver chloride} = 0.6057 \text{ gm.}$$

Very many chemical calculations are variations of the above types.

## CHAPTER 9

# THE CLASSIFICATION OF THE ELEMENTS

The primary object of classification is to arrange the facts so that we can acquire the greatest possible control over them with the least possible effort.

The periodic law has given to chemistry that prophetic power long regarded as the peculiar dignity of its sister science, astronomy.—H. C. BOLTON.

### § 1 Early Attempts at Classification; Döbereiner's Triads— Newlands's Law of Octaves

It is sometimes argued that consideration of the Classification of the Elements should be deferred until after the evidence for their electronic structure has been studied. In view of the not inconsiderable extent to which knowledge of the Periodic Table has contributed to the elucidation of these electronic structures and of the fact that the conclusions have been summarized already in Chapter 2 the reverse order has been adopted here.

In Chapter 1 (page 4) it was explained that the method of science consists of four stages, the second of which is "classification and comparison of facts." The urge to classify or to sort things out into divisions or compartments is a natural one. To attempt to classify the elements is thus the result of a natural impulse and it has long been an attractive subject. Many such attempts have been made such as classification into metals and non-metals; into acidic and basic, or, what amounts to the same thing, into electronegative and electropositive elements (see page 216); they have been classed according to their valency and also according to many other properties. In all these systems an element appeared in more than one class; or elements with but few properties in common were grouped together.

In all chemical changes one property remains unaltered and the only successful system of classification has been based on this property, viz., at first, the Atomic Weights of the elements, and later the Atomic Numbers for, as already stated (page 14) the Atomic Weight is now known to be, approximately, proportional to the really fundamental property, the Atomic Number.

Between 1816 and 1829, J. W. Döbereiner noticed regularities in the atomic weights of certain related elements, for he found that most of the then known chemically related elements either had almost the same atomic weight—e.g., iron, cobalt, and nickel—or else exhibited a constant difference when arranged in sets of three.

Thus, rounding off modern atomic weights:

	Calcium	Strontium	Barium
Atomic Weight	40	87	137
Difference	47	50	
	Chlorine	Bromine	Iodine
Atomic Weight	35.5	80	127
Difference	44.5	47	
	Sulphur	Selenium	Tellurium
Atomic Weight	32	79	128
Difference	47	49	

These were called Döbereiner's Triads, but it was soon felt that his list was but a fragment of a more general law. Between 1863 and 1866, J. A. R. Newlands published a series of papers in which he arranged the elements in the ascending order of their atomic weights, and noticed that every succeeding eighth element was "a kind of repetition of the first." Thus:

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe

. . . . .

"In other words," said Newlands, "members of the same group of elements stand to each other in the same relation as the extremities of one or more octaves in music. This peculiar relationship I propose to term provisionally **the law of octaves**." Newlands noticed that elements belonging to the same group "usually" appeared in the same column, and he declared that all the numerical relations which had been observed among the atomic weights, "including the well-known triads, are merely arithmetical results flowing from the existence of the law of octaves."

The "law of octaves" did not attract much attention, probably because faulty atomic weights seriously interfered with the arrangement.\* Similar remarks apply to some papers by A. E. B. de Chancourtois in 1862, where also it was proposed to classify the elements by their atomic weights.

## § 2 The Periodic Law—D. I. Mendeléeff and L. Meyer

D. I. Mendeléeff and L. Meyer, quite independently and, so far as we can tell, quite in ignorance of Newlands's and Chancourtois's work, obtained a far clearer vision of the "law of octaves" about 1869. Mendeléeff said: "When I arranged the elements according to the

\* When Mr. Newlands read a paper on "The Law of Octaves" at a meeting of the London Chemical Society in 1866, Prof. G. C. Foster said that any arrangement of the elements would present occasional coincidences, and inquired if Mr. Newlands had ever examined the elements according to their initial letters. Twenty-one years later the Royal Society awarded Newlands the Davy Medal for his discovery.

magnitude of their atomic weights, beginning with the smallest, it became evident that there exists a kind of periodicity in their properties." Otherwise expressed, if the elements be arranged in the order of increasing atomic weights, their *properties* vary from member to member in a definite way, but return more or less nearly to the same value at fixed points in the series. Mendeléeff continued: "I designate by the name 'periodic law' the mutual relations between the properties of the elements and their atomic weights, these relations are applicable to all the elements, and have the nature of a periodic\* function." Expressed more concisely, we have **Mendeléeff's periodic law: The properties of the elements are a periodic function of their atomic weights.**

Consequently, Mendeléeff was able to construct a table in which the elements were arranged horizontally in order of their atomic weights and vertically according to their resemblances in properties. The early tables were very imperfect on account of the unreliability of many atomic weights, as then assigned, but they were afterwards amended and modified in the light of the more accurate data which became available. The table on page 125 shows Mendeléeff's scheme modified so as to conform with modern knowledge (Table VII).

Mendeléeff's table was constructed on the basis of the atomic *weights* of the elements, but the properties of the elements are in reality a periodic function of an even more fundamental number than the atomic weight, viz., the **Atomic Number**. This will be discussed fully in Chapter 10—for the present it may be defined as *the ordinal number of the element in the periodic table of Mendeléeff*. Mendeléeff reversed the order of certain pairs of elements, as indicated by the values of their atomic weights, in order to bring them into their proper places (as determined by their properties). This procedure has been abundantly justified, and the Periodic System as a whole placed on a firm, theoretical basis by recent discoveries concerning the structure of the atom. Table VII accordingly includes the values of the Atomic Numbers, as well as of the Atomic Weights.

### § 3 General Structure of the Periodic Table

Beginning with hydrogen, the element of lowest atomic weight, and writing down the elements in a horizontal row in the order of their atomic weights, we come to elements showing a recurrence of the properties of elements already written down, at intervals of 2, 8, 8, 18, 18 and 32 elements respectively. If we start a new line in the table at each of these recurrences, that is with the beginning of each new period, we shall find the elements arranged vertically in *families* or *groups* of like chemical properties. In the table the groups are numbered from I to VIII with the addition of Group O as shown.

\* A periodic function is one whose value repeats itself at regular intervals. The interval is called a "period."

Periods	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII	Group O
I (short)	A H(1) 1-0080	B —	A —	A —	A —	A —	A H(1) 1-0080	—	H(2) 4-003
II (short)	A Li(3) 6-94	B Be(4) 9-013	B B(5) 10-82	B C(6) 12-011	B N(7) 14-008	B O(8) 16-00	B F(9) 19-00	—	Ne(10) 20-183
III (short)	A Na(11) 22-991	B Mg(12) 24-32	B Al(13) 26-98	B Si(14) 28-09	B P(15) 30-975	B S(16) 32-066	B Cl(17) 35-457	—	A(18) 39-98
IV (long)	A K(19) 39-100 Cu(29) 63-54	B Ca(20) 40-08 Zn(30) 65-38	A Sc(21) 44-96 Ga(31) 69-72	A Ti(22) 47-90 Ge(32) 72-60	A V(23) 50-95 As(33) 74-91	A Cr(24) 52-01 Se(34) 78-96	A Mn(25) 54-94 Br(35) 79-916	Fe(26) 55-85 Co(27) 58-94 Ni(28) 58-71	—
V (long)	A Rb(37) 85-48 Ag(47) 107-88	B Sr(38) 87-63 Cd(48) 112-41	A Y(39) 88-92 In(49) 114-82	A Zr(40) 91-22 Sn(50) 118-70	A Nb(41) 92-91 Sb(51) 121-76	A Mo(42) 95-95 Te(52) 127-61	A Tc(43) — I(53) 126-91	Ru(44) 101-1 Rh(45) 102-91 Pd(46) 106-4	Kr(36) 83-80
VI (long)	A Cs(55) 132-91	B Ba(56) 137-36	A La(57) 138-92 Ce(58) 140-13 Pr(59) 140-92 Nd(60) 144-27 Pm(61) — Sm(62) 150-35 Eu(63) 152-0 Gd(64) 157-26 Tb(65) 158-93 Dy(66) 162-51 Ho(67) 164-94 Er(68) 167-27 Tm(69) 168-94 Yb(70) 173-04 Lu(71) 174-99 Ti(81) 204-39	A Hf(72) 178-6 Pb(82) 207-21	A Ta(73) 180-95 Bi(83) 209-00	A W(74) 183-86 Po(84) —	A Re(75) 186-22 At(85) —	Os(76) 190-2 Ir(77) 192-2 Pt(78) 195-09	Xe(54) 131-3
VII	A Fr(87) —	B Ra(88) 226-05	A Ac(89) —	A Th(90) 232-05	A Pa(91) 231	A U(92) 238-07	—	—	Rn(86) 222

Groups VIII and O are unusual in that they are alternatives. The Periods are numbered 1, 2, etc., up to 7; the first three are known as *short* periods, the others as *long* periods. In the long periods the groups are subdivided into two sub-groups, differentiated in the table by being placed to the left or right respectively in their appropriate columns. These are designated *A* and *B* respectively.

In periods 4 and 5 (the first of the long periods) it is necessary, as we have seen, to pass not 8 but 18 elements, before one of really similar properties is reached. Thus potassium is an alkali metal closely related to sodium, the first element of the second short period. The next alkali metal is rubidium. Of the elements which lie between potassium and rubidium (that is, the elements of the first long period) the ten elements scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, are of a new type not hitherto met with. They are placed in separate sub-groups, and three of them, viz., iron, cobalt and nickel, are placed in a group by themselves (Group VIII) as they are clearly too closely related to be placed in separate groups. These elements are called *transition* elements and they are thus interposed between the eight elements typical of the groups as represented in the short periods. This is easily seen if we disregard these transition elements for the moment, for we then have the sequence

K, Ca, Ga, Ge, As, Se, Br, Kr,

which closely resembles the previous short period, which is

Na, Mg, Al, Si, P, S, Cl, A.

A similar phenomenon is to be found in the second long period, but in the third long period a new feature is seen in the remarkable series of fourteen elements known as the rare earths; a series which is inserted, as it were, among the transition elements in the same kind of way as the transition elements are inserted into the typical elements. They constitute a series of distinct elements, having yet very similar properties, and are responsible for the expansion of this period from 18 to 32 elements.

These relationships between the groups, periods, transition elements and rare earths are well brought out in the form of the Periodic Table shown in Table VIII (page 127). It emphasizes also the relationship, and yet the individuality, of the sub-groups—the typical and transitional elements.

Many other ways of writing the Periodic Table have been proposed; two recent ones which have considerable merit are those suggested by T. S. Wheeler (1947), based on external electronic configurations, and by R. F. Wheeler (1955), in which the periods are arranged in vertical columns and the groups in horizontal rows instead of vice versa (Table IX). This scheme like Thomsen's form of the Table makes inclusion of the Rare Earths easier, and also serves to diminish the emphasis formerly placed upon the division into sub-groups A and B and the isolation of Group 8 from its proper sequence.





In four instances the order assigned to the elements departs from that of the atomic weights. These are the four pairs of elements: argon and potassium, cobalt and nickel, tellurium and iodine, thorium and protoactinium. In each case the order, as determined by the atomic weights, is reversed so that these elements may fall into the places in the Periodic Table to which their properties rightly assign them.

TABLE IX.—THE PERIODIC TABLE OF THE ELEMENTS (R. F. WHEELER)

Group								Group
1	1 H	→3 Li	11 Na	19 K	37 Rb	55 Cs	87 Fr	1
2		4 Be	12 Mg	→20 Ca	38 Sr	56 Ba	88 Ra	2
T 1				21 Sc	39 Y	→57 La	89 Ac	T 1
						59 Pr	91 Pa	
						60 Nd	92 U	
						61 Pm	93 Np	
						62 Sm	94 Pu	
						63 Eu	95 Am	
						↓64 Gd	96 Cm	
						65 Tb	97 Bk	
						66 Dy	98 Cf	
						67 Ho	99 E	
						68 Er	100 Fm	
						69 Tu	101 Mv	
						70 Yb	102 No	
						→71 Lu	103	
T 2				22 Ti	40 Zr	72 Hf	104	T 2
T 3				23 V	41 Nb	73 Ta	105	T 3
T 4				24 Cr	42 Mo	74 W	106	T 4
T 5				25 Mn	43 Tc	75 Re	107	T 5
T 6				26 Fe	44 Ru	76 Os	108	T 6
T 7				27 Co	45 Rh	77 Ir	109	T 7
T 8				28 Ni	46 Pd	78 Pt	110	T 8
T 9				29 Cu	47 Ag	79 Au	111	T 9
T 10				→30 Zn	48 Cd	80 Hg	112	T 10
3		5 B	13 Al	31 Ga	49 In	81 Tl	113	3
4		6 C	14 Si	32 Ge	50 Sn	82 Pb	114	4
5		7 N	15 P	33 As	51 Sb	83 Bi	115	5
6		8 O	16 S	34 Se	52 Te	84 Po	116	6
7		→9 F	17 Cl	35 Br	53 I	85 At	117	7
0	2 He	10 Ne	18 Ar	36 Kr	54 X	86 Rn	118	0

This was done for the first three pairs by Mendeléeff himself, who believed that subsequent determinations would show that the atomic weights then accepted were inaccurate, and that when known, the true values would fall into the order of the Periodic Table.

Many redeterminations of the atomic weights of these elements have been made in consequence; but have failed to indicate that the atomic weights of these elements as usually accepted are seriously in error. Nevertheless, Mendeléeff's vision has been abundantly justified by more recent discoveries which have shown the significance of the *atomic number*, to which the atomic weight is approximately proportional, and have also demonstrated the existence of isotopes; that is,

atoms of slightly different mass, but identical properties and atomic number (see Chapter 10).

Most of the well-defined physical and chemical properties of the elements are periodic—valency, specific gravity, atomic volume, melting point, hardness, malleability, ductility, compressibility, coefficient of expansion, thermal conductivity, latent heat of fusion, refraction equivalents for light, colour, electrical conductivity, magnetic power, etc. When the numerical values of these properties and the atomic weights of the elements are tabulated on squared paper, a curve is obtained which is broken up into periods.

This is particularly well illustrated by the curve showing the relationship between atomic volume and atomic weight, to which attention was first drawn by Lothar Meyer. The atomic volume is the quotient

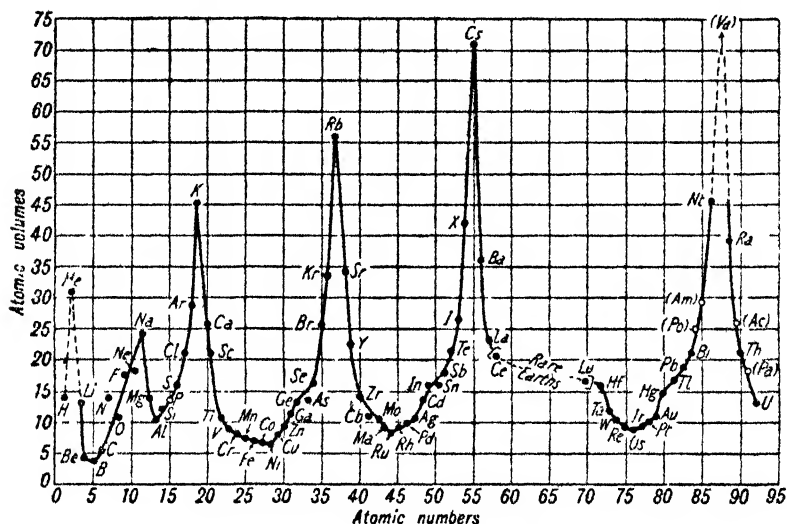


FIG. 9.1.—Relation between Atomic Volumes and Atomic Numbers

obtained by dividing the atomic weight of an element by its specific gravity in the solid condition. When the atomic volumes of the elements are plotted against the atomic numbers, a periodic curve is obtained, as illustrated in Fig. 9.1.

#### § 4 The Gaps in Mendeleeff's Tables

Mendeleeff considered it necessary to leave gaps in the table, for undiscovered elements, and more particularly in order to keep certain related elements in the same vertical column. Mendeleeff boldly prophesied that the **missing elements** would be discovered later, and in

some cases even predicted their properties in considerable detail. For instance, when Mendeléeff announced the law, there were two blank spaces in group III—the missing elements were called **eka-aluminium** and **eka-boron** respectively; and another space below titanium in group IV—the missing element in this case was called **eka-silicon**. The hypothetical character of these elements was considered to be an inherent weakness of the law, but the weakness was turned to strength when gallium, scandium, and germanium subsequently appeared duly clothed with those very properties which fitted closely with Mendeléeff's audacious prognostications. This hit attracted considerable attention, and served to strengthen the faith of chemists in the fundamental truth of the periodic law. In illustration, the case of eka-silicon and germanium is quoted side by side in Table X.

The confirmations of Mendeléeff's predictions of the properties of eka-aluminium (gallium) and of eka-boron (scandium) were equally striking.

### § 5 The Applications of the Periodic Law

Mendeléeff pointed out that the periodic law could be employed in: (1) the estimation of the atomic weights of elements not fully investigated; (2) the prediction of the properties of hitherto unknown elements; and (3) The correction of atomic weights, as well as for the classification of the elements.

**1. The estimation of the atomic weights of the elements.** On account of practical difficulties, it is not always possible to fix the atomic weights of some elements by vapour density determinations (Avogadro's rule), and by specific heat determinations (Dulong and Petit's rule), and the atomic weights of these elements were frequently assigned on somewhat uncertain grounds.

The application of the Periodic System to the alteration of the atomic weight of indium has already been mentioned (Chapter 7, page 102). Other similar changes have been made analogously. Thus, beryllium, uranium, and a number of the rare earths at one time did not fit very well into the table, but Mendeléeff's alteration of the supposed atomic weights to make these elements fit the table was subsequently justified by vapour density determinations of the volatile chlorides, or by specific heat determinations.

**2. The prediction of the properties of hitherto undiscovered elements.** Some instances of Mendeléeff's predictions of the properties of undiscovered elements, and the subsequent verifications of these predictions, have been given above.

In order to avoid introducing new names when speaking of unknown elements, Mendeléeff designated them by prefixing a Sanscrit numeral—eka (one), dwi (two), tri (three), etc.—to the names of the next lower analogous elements of the odd or even numbered series of the same group.

In addition to the prediction of germanium, gallium, and scandium

already discussed, Mendeléeff foretold the possible discovery of eka-and dwi-caesium; eka-niobium—En = 146; of eka-tantalum—Et = 235; of dwi-tellurium—Dt = 212; and of the analogues of manganese: eka-manganese—Em = 100; and tri-manganese—Tm = 190.

TABLE X.—COMPARISON OF PREDICTED AND OBSERVED PROPERTIES OF GERMANIUM

Eka-silicon, Es (predicted in 1871)	Germanium, Ge (discovered in 1886)
Atomic weight, 72.	Atomic weight, 72.6.
Specific gravity, 5.5	Specific gravity, 5.47.
Atomic volume, 13.	Atomic volume, 13.2.
Element will be dirty grey, and on calcination will give a white powder of $\text{EsO}_2$ .	The element is greyish-white and on ignition furnishes a white oxide $\text{GeO}_2$ .
Element will decompose steam with difficulty.	The element does not decompose water.
Acids will have a slight action, alkalis no pronounced action.	The element is not attacked by hydrochloric acid, but it is attacked by aqua regia. Solutions of KOH have no action, but the element is oxidized by fused KOH.
The action of sodium on $\text{EsO}_2$ or on $\text{EsK}_2\text{F}_6$ will give the element.	Germanium is made by the reduction of $\text{GeO}_2$ with carbon, or of $\text{GeK}_2\text{F}_6$ with sodium.
The oxide $\text{EsO}_2$ will be refractory and have a sp. gr. 4.7. The basic properties of the oxide will be less marked than $\text{TiO}_2$ and $\text{SnO}_2$ , but greater than $\text{SiO}_2$ .	The oxide $\text{GeO}_2$ is refractory and has a sp. gr. 4.703. The basicity is very feeble.
Eka-silicon will form a hydroxide soluble in acids, and the solutions will readily decompose forming a metahydrate.	Acids do not precipitate the hydrate from dilute alkaline solutions, but from concentrated solutions, acids precipitate $\text{GeO}_2$ or a metahydrate.
The chloride $\text{EsCl}_4$ will be a liquid with a boiling point under $100^\circ$ and a sp. gr. of 1.9 at $0^\circ$ .	Germanium chloride, $\text{GeCl}_4$ , boils at $86^\circ$ , and has a sp. gr. at $18^\circ$ , 1.887.
The fluoride $\text{EsF}_4$ will not be gaseous.	The fluoride $\text{GeF}_4 \cdot 3\text{H}_2\text{O}$ is a white solid mass.
Eka-silicon will form a metallo-organic compound $\text{Es}(\text{C}_2\text{H}_5)_4$ boiling at $160^\circ$ , and with a sp. gr. of 0.96.	Germanium forms $\text{Ge}(\text{C}_2\text{H}_5)_4$ , which boils at $160^\circ$ , and has a specific gravity slightly less than water.

The case of the so-called **inert gases** is of more recent date. The discovery of argon and helium could not have been predicted from Mendeléeff's Periodic Law, but after these elements had been discovered, and accommodated in the periodic table between the strongly acid halogen family and the strongly basic alkali metals, the probable existence of other similar inert gases was indicated. When an exhaustive search was made, krypton, neon, and xenon were discovered with properties and atomic weights which could have been predicted from the arrangement made for argon and helium in Mendeléeff's table.

**3. The correction of the values of atomic weights.** If the atomic weight of an element does not fit with the regular course of, say, the atomic volume curve, Fig. 9.1, the atomic weight is probably in error. Thus, the atomic weights of platinum, iridium, and osmium at that time were probably too high, and subsequent determinations verified this inference. Thus the atomic weights of these elements were:

	Platinum	Iridium	Osmium
In 1870 . . .	196.7	196.7	198.6
In 1940 . . .	195.23	193.1	190.2

Similar attempts to correct atomic weights such as those of iodine and tellurium have not been so successful as mentioned above, and as will be seen in the next chapter, the most recent investigations have indicated that in this respect the applicability of the Periodic Law is not quite so wide as was thought by Mendeléeff.

### § 6 Defects in the Periodic Law

The Periodic Table in its original application suffered from some defects. The most important of these were:

the allocation of hydrogen;

the allocation of the rare earths;

the fact that, according to the Periodic Law, the existence of two elements with different properties and approximately the same Atomic Weights should be impossible;

some elements (e.g., copper and the alkali metals) were allocated places in the Periodic Table in opposition to their properties, while some elements (e.g., copper and mercury, silver and thallium) which appear to be chemically similar are separated in the Table.

All these difficulties are now thought to be solved or are felt to be of minor importance when they are considered in the light of the electronic theory of the structure of the atom, now to be discussed (Chapter 10).

## CHAPTER 10

# THE CONSTITUTION OF MATTER

The electron has conquered physics, and many worship the new idol rather blindly.—H. POINCARÉ (1907).

Even if we resolve all matter into one kind, that kind will need explaining, and so on for ever and ever deeper and deeper into the pit at whose bottom truth lies, without ever reaching it, for the pit is bottomless.—O. HEAVISIDE.

### § 1 General

IN Chapter 2 the development of modern ideas about the nature of matter, the structure of the atom and the way in which this structure accounts for chemical behaviour has been outlined. In the intervening chapters the development of chemical theory previously to the discovery of radioactivity and the electron has been described; it is now important to discuss the *experimental basis* for the present theories of the nature of matter which were summarized in Chapter 2.

From the earliest times men have hankered after some simplifying generalization which would co-ordinate the multitudinous variety of material substances by ascribing to them a common origin, or by building them up from some single form of matter or potential matter.

This tendency was marked among the earlier Greek philosophers and the suggestion arose of a *prima materia* ("potential matter") which was supposed to consist of parts which, when grouped in different ways, produced the various kinds of matter considered by them to be elemental.

Many suggestions have been made as to the nature of this primal element; at various times air, fire, earth, and water were so suggested. A more modern suggestion of this kind, which commanded considerable attention, was due to Prout (1816) and is known as Prout's hypothesis. This states that the elements are different aggregates of the atoms of primordial hydrogen; in consequence, within the limits of experimental error, the atomic weights of the different elements should be expressible by whole numbers when the atomic weight of hydrogen is unity.

Many writers, attracted by its apparent simplicity, gave unqualified support to Prout's hypothesis; but an impartial review of the facts, with very much more refined data than were available in Prout's day, led J. S. Stas (1860-5) to state: "I have arrived at the absolute conviction, the complete certainty, so far as is possible for a human being to attain to certainty in such matters, that the law of Prout is nothing but an illusion, a mere speculation definitely contradicted by experience."

Although Prout's hypothesis in its original form did not survive the test of an impartial examination in the light of experimentally determined facts, the discovery of the Periodic Law by Mendeléeff, soon after the publication of this pronouncement by Stas, served to direct men's minds afresh to the problem presented by the circumstance that the clearly demonstrated *relationship* among elements might well imply a common origin, or common basis, for them all.

Other well-known facts pointed in the same direction. Thus, although it is true that a great many elements have atomic weights which are not even approximately whole numbers, nevertheless many of them, too many to be the result of chance, are very close to whole numbers. In the International Table of Atomic Weights for 1955, which contains ninety-nine elements, fifty-one have atomic weights which are whole numbers within one-tenth of a unit. Again, it is a significant fact that closely related elements are very often found associated

together in nature, for they are often not widely distributed, nor do they as a rule have any marked chemical affinity for each other. Other evidence is also afforded by the regularities observable in the grouping of spectral lines, the results of the investigation of the discharge of electricity through rarefied gases and the study of radioactivity.

### § 2 Electric Discharge in Rarefied Gases

Under ordinary conditions, gases are such poor conductors of electricity that they are classed as good insulators. In order to get electricity to pass through air at ordinary atmospheric pressures, a voltage approaching 30,000 volts per cm. is required; but as the pressure of the air is diminished the voltage required to produce a discharge diminishes in almost exactly the same proportion.

At low pressures (0.03 mm.) the discharge takes the form of a blue glow proceeding from the cathode (or negative electrode) in a course perpendicular to the cathode, and independent of the exact position of the anode. When it strikes the glass a green fluorescence is produced. These "rays," proceeding from the cathode, were named **cathode rays** by Goldstein in 1876, but previously Plucker (1858) had observed that they can be deflected from their course by a magnet showing that they are electrically charged. Also, W. Hittorf (1869) found that if a solid body—say a Maltese cross made of mica—be placed between the anode and cathode, a true shadow appears on the glass, the shape of the cross shows that *the cathode rays travel in straight lines normal to the surface of the cathode, and they will cast a well-defined shadow if a solid object be placed between the cathode and the wall of the vacuum tube.* A wheel also, as was shown by Crookes in 1879, may be caused to rotate by allowing the cathode rays to strike against its vanes, and a number of minerals glow, or phosphoresce, when acted upon by these cathode rays. Further, by the use of a concave cathode the rays may be brought to a focus and a substance such as a metal can be raised to incandescence, or even melted, by being placed there.

If the exhaustion of the tube in which the cathode rays are being produced is carried to the limit, the discharge ceases altogether and the current from the induction coil is no longer able to pass through the tube.

The fact that the tube when highly evacuated is non-conducting shows that *the electric current must somehow be carried from one electrode to the other by something.*

The fact already mentioned that the cathode rays can be deflected by a magnet indicates that they consist of charged particles of some sort. Perrin in 1895 was able to show that they are negatively charged by arranging a vacuum tube so that the cathode stream passed into a small metal cylinder inside the tube, and, by means of a wire, he connected the inner cylinder with an external electroscope. The electroscope acquired a gradually increasing negative charge, or a positively charged electroscope was discharged.

In 1879 Crookes suggested that the cathode rays consisted of particles or molecules of a fourth state of matter—an ultra-gaseous state called radiant matter. Lenard was able to show in 1894 that the cathode rays could pass through thin sheets of metal (but not through thick ones), and in August 1897, J. J. Thomson suggested the startling hypothesis that what Crookes called "radiant matter" or the cathode rays, is a stream of negatively charged particles or corpuscles which have been formed by the disintegration of atoms of the gas in the vacuum tube. The term **electron** had been applied by G. J. Stoney (1881) to designate the unit or atomic charge of electricity, and it is now used for the sub-atomic particles which stream from the negative electrode when a discharge is passing through an attenuated gas. No difference can be detected in the corpuscles derived from different gases, nor can any difference be detected in the properties of these electrons from whatever source they are obtained (they are now known to be emitted by heated metals, by the action of ultra-violet light on metals and by some chemical reactions) and hence it is inferred that **the electrons are common constituents of all matter.**



Thomson, by comparing and measuring the deflections produced in the path of a stream of electrons by magnetic and by electric fields, was able to determine the ratio of the charge to the mass (usually represented by  $e/m$ ) and found it to be  $1.2 \times 10^7$  electromagnetic units per gram. Later more accurate determinations have led to the value  $1.758 \times 10^7$  e.m.u. per gm. This value was subsequently found to be substantially constant irrespective of the source of the electron, provided that its speed (which can vary over a very wide range, an average value being 20,000 miles per sec.) did not approach that of light when the "mass" of the electron increases with its velocity.

This value for the ratio  $e/m$  is about 1,836 times that of a hydrogen ion in electrolysis (see Chapter 15), from which it follows either (i) that the mass of the electron is  $\frac{1}{1836}$ th of that of the hydrogen atom, but carries the same charge as a hydrogen ion, or (ii) the masses are the same while the charge on the electron is 1,836 times that of a hydrogen ion. Experiment has decided in favour of the former alternative.

These results led naturally to the hypothesis that the constitution of matter is electronic in nature; that is, that the atom has a structure involving, *inter alia*, electrons.

### § 3 X-rays or Röntgen Rays

When the exhaustion of a vacuum tube is such that the tube is on the verge of becoming electrically non-conducting, and the glass opposite the cathode is brilliantly fluorescent, rays proceed from the fluorescent glass, *outside the tube*; these rays—called **X-rays** or **Röntgen rays**—have quite different properties from the cathode or Lenard rays, because they will pass through glass, and they are not deflected by a magnet.

Röntgen rays are produced by the destruction of the cathode rays and are formed when the cathode rays impinge on solid objects. Every substance when bombarded by electrons emits Röntgen rays—the glass walls of a vacuum tube, heavy metals like platinum or uranium, etc. These so-called X-rays are capable of penetrating freely through paper, wood, aluminium and flesh, but are absorbed by lead, platinum or bone. They can excite fluorescence on a paper screen coated with barium platinocyanide,  $\text{BaPt}(\text{CN})_4$ , or calcium tungstate,  $\text{CaWO}_4$ ; they can fog a photographic plate; and make the air through which they pass a conductor of electricity, and, as noted, have a remarkable power of penetrating substances opaque to ordinary light. Their penetrating power varies according to the degree of exhaustion of the tube from which they are being produced. Thus Röntgen radiations with a lower penetrative power, called *soft rays*, are emitted from a vacuum tube which has too much residual air. The supply of electrons is then plentiful; their speed is comparatively slow; and a current of comparatively low electromotive force is needed. Conversely, radiations with a high penetrative power, called *hard rays*, are emitted if the tube be very highly exhausted. The supply of electrons is then relatively small; their speed is comparatively high; and the necessary electromotive force is high.

These Röntgen rays consist of electromagnetic waves similar to those of ordinary light, but of very much smaller wave-length.

For some time after their discovery, in 1895, it was not possible to detect, in the case of X-rays, one very characteristic property of a wave motion, in that it was not possible, on account of their extremely small wave-length, to obtain evidence of their diffraction by matter. This was at length accomplished by Laue, and by Friedrich and Knipping (1912), when they showed that X-rays suffer diffraction on passage through a crystal.

Before this time, crystallographers had come to the conclusion, from the study of the general properties of crystals themselves, that in a crystal the constituent particles are arranged at the points of different lattice structures, although they had not then decided the nature of the particles occupying the lattice points. (Cf. Chapter 13, pages 196 *et seq.*)

On the basis of this conception, it is possible to calculate from a knowledge of the density of a simple crystal such as rock-salt, the atomic weights of the atoms

present and the Avogadro Number (page 85), the distances between the planes of particles in the crystal, and the result of Laue's and of Friedrich and Knipping's experiments shows that these distances are commensurate with the wave-length of the X-rays employed. Their results also serve to confirm the space-lattice theory of crystal structure, and in the hands of W. H. and W. L. Bragg and others the correctness of this theory has been demonstrated and the structures of many crystals have been worked out. This aspect of the diffraction of X-rays is more fully treated in Chapter 13—for the moment the important fact is that, as Bragg showed, they suffer reflection at definite angles of incidence in the same way as light from a diffraction grating; thus providing a means for the analysis of X-rays themselves.

In this way it has been found that the rays emitted from an ordinary X-ray tube are usually heterogeneous, mixed hard and soft, but C. G. Barkla (1906) showed that if the exciting stimulus be great enough, every substance can be made to emit a set of X-rays which can be regarded as homogeneous and characteristic, in that the absorption coefficient,  $k$ , of the radiations from that substance, in some standard substance (say aluminium), is a constant, e.g.:

	Ca	Cr	Cu	Se	Ag	Ba
$k$	435.0	136.0	47.7	18.9	2.5	0.8

Elements with atomic weights between aluminium and silver emit two sets of these homogeneous characteristic radiations, e.g., palladium emits two charac-

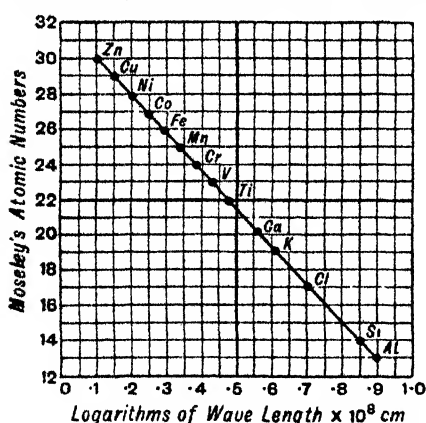


FIG. 10.1.—Relation between the Wave-length of the Characteristic X-ray of the Elements and the Atomic Number

teristic sets of homogeneous rays with wave-lengths respectively  $0.58 \times 10^{-8}$  and  $0.51 \times 10^{-8}$  cm., and nickel,  $1.66 \times 10^{-8}$  and  $1.50 \times 10^{-8}$  cm. respectively. H. G. J. Moseley (1913) further showed that although, when the increase in the atomic weight of the element is plotted against the corresponding decrease in wave-length, the curve does not run smoothly; if the logarithms of the wave-lengths or vibration frequencies be plotted against a series of natural numbers, the curve runs quite smoothly. This is illustrated by Fig. 10.1. Moseley demonstrated that the X-ray spectrum of every element from aluminium to gold is related in this way to an integer  $N$  called the **atomic number** ranging from 13 for aluminium to 79 for gold, some blanks being introduced corresponding to unknown elements. The order of the atomic numbers is the same as the order of the atomic weights, except where the latter disagrees with the order of the chemical properties, so that the atomic number in the periodic table is a more fundamental index of quality than the atomic weight. Thus the **wave-length**, or the **vibration frequency**, of the characteristic X-rays from different elements changes from element to element by regular jumps.

The wave-length of the characteristic X-rays of an element thus depends upon, and gives us a measure of, some fundamental property of the atom whose numerical value varies by one unit as we pass from atom to atom in the order of the Periodic Table. This number (that is, the ordinal number indicating the position of an element in the Periodic Table) is called the **Atomic Number**.

#### § 4 Radioactivity

The significance of the Atomic Number and the nature of the fundamental property of which it is the index have been greatly elucidated by the study of the phenomena of radioactivity, which has furnished further striking confirmation of the view (resulting from the discovery of the electron) that the atom is complex.

In 1896 Becquerel found that some substances, notably uranium minerals, and uranium salts in general, give out rays which are capable of affecting a photographic plate, even when the plate is protected with a layer of black paper, and Niepce had observed, thirty years before, that uranium salts could affect photographic plates in the dark. Thorium compounds were shown shortly afterwards to possess similar properties, and such substances have been termed **radioactive** from their property of emitting these radiations.

##### *Discovery of Radium*

The examination of a number of uranium minerals by Madame Curie indicated that some of these minerals gave radiations of greater intensity than the purified uranium which they contained, and she was thus led to suspect the presence of a radioactive substance of much greater activity than uranium itself. Upon investigation she was able to isolate a salt of a new element, of a very much more active character than uranium, to which the name **radium** was given.

##### *The Nature of the Radiations*

Radioactive substances were found in general to be detectable in three ways, viz.:

- (i) by the action on a photographic plate;
- (ii) by the phosphorescence produced from certain minerals such as zinc blende;
- (iii) by making the air in their neighbourhood capable of conducting electricity (thus causing, for example, the discharge of an electroscope).

Careful investigation shows that the rays emitted are of **three** kinds, which are known as  $\alpha$ -rays,  $\beta$ -rays and  $\gamma$ -rays. By examining their behaviour when acted upon by powerful magnetic fields and when sheets of metal foil are interposed in their path, the nature of these rays has been shown to be as follows:

- (i)  $\alpha$ -rays. These consist of positively charged particles, which are easily absorbed by thin sheets of metal foil and have a limited range in air.
- (ii)  $\beta$ -rays. These are negatively charged particles, identical with the electron, emitted with a speed comparable with that of light, and able to penetrate thin sheets of aluminium.
- (iii)  $\gamma$ -rays. These are unaffected by magnetic fields and consist of X-rays of very short wave-length. They are capable of penetrating a layer of lead several centimetres in thickness.

The  $\alpha$ -rays, or  $\alpha$ -particles, have further been found to have a mass of 4 units (compared with a hydrogen atom as unity) and have been shown by Rutherford to be atoms of helium, each carrying a positive charge equal in magnitude to *twice* the negative charge of an electron. These  $\alpha$ -particles are projected at high velocities (one-fifteenth to one-tenth of that of light).

The identity of the  $\alpha$ -particle as a charged atom of helium is a fact of great significance and importance in the further elucidation of the structure of the atom. The experimental proof was provided by Rutherford and his co-workers. Rutherford and Royds (1908) sealed radon (radium emanation, below) in a very thin-walled glass tube (through which  $\alpha$ -particles were able to pass) and this tube was itself sealed inside another tube which was exhausted until an electric discharge would not pass through it. The whole apparatus was left for a time after which it was found that a discharge would now pass and the helium spectrum could be observed.

Rutherford (1905) also determined the ratio of the charge to the mass of an  $\alpha$ -particle and found it to be  $4.82 \times 10^4$  coulombs per gm., which is almost exactly half of the corresponding ratio for the hydrogen ion ( $9.65 \times 10^4$  coulombs per

gm.). Rutherford and Geiger (1908) found the charge on an  $\alpha$ -particle by measuring the total charge carried by a counted number of  $\alpha$ -particles (the counting being done by means of the scintillations caused by the impact of the  $\alpha$ -particles on a fluorescent screen). The value of the charge so found was  $3.1 \times 10^{-19}$  coulombs which in conjunction with the charge/mass ratio leads to the value  $0.66 \times 10^{-28}$  gm. for the mass of the  $\alpha$ -particle which is almost exactly four times that of a hydrogen atom ( $1.6 \times 10^{-24}$  gm.).

Careful investigation has revealed the fact that the emission of these radiations takes place at a rate which is entirely and absolutely independent of the external physical conditions. Thus, for example, the activity of radium is exactly the same at the temperature of liquid air as it is at a red heat. This is completely different from ordinary chemical change, the rate of which varies with temperature.

Another remarkable fact which soon became apparent is that the emission of these radiations is accompanied by the change of the element concerned into another element. Thus, for example, radium is undoubtedly an element; it has a definite atomic weight and spectrum, and a definite place in the Periodic Table. It is constantly changing, however, at an absolutely characteristic (and so far as we are concerned) unalterable rate with the emission of an  $\alpha$ -particle (a charged helium atom) and the formation of a radioactive gas known as niton, or radon. This gas, a typical inert gas, is, in the same sense as radium, an element. In its turn, radon, too, undergoes a radioactive transformation. Investigation has shown that radioactive changes take place in this way in series, the final non-radioactive product of these series being lead. Three such series of naturally occurring radio-elements have been distinguished, known respectively as the Uranium, the Thorium and the Actinium series from the names of the elements of highest atomic weight in each. At each stage the change may be accompanied by the emission of an  $\alpha$ -particle or by the formation of a  $\beta$ -particle along with  $\gamma$ -rays.  $\alpha$ -particles and  $\beta$ -particles are never emitted together in one single change.

#### *The Disintegration Hypothesis*

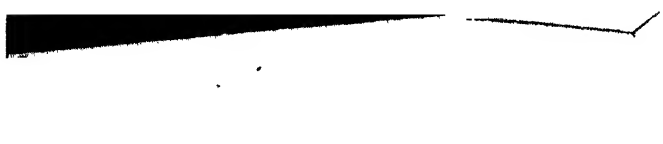
Radioactive changes are clearly atomic phenomena, since they are entirely unaffected either by reagents or the physical conditions, and are unchanged even by the formation of compounds of the element concerned. To account for these and other facts of radioactivity, Rutherford and Soddy in 1903 put forward the theory of spontaneous disintegration. According to this theory the atom of a radioactive element is a complex structure, potentially unstable, and spontaneous disintegration occurs at a rate dependent upon, and characteristic of, the nature of the element concerned, with the emission from the atom itself, either of an  $\alpha$ -particle or a  $\beta$ -particle and the simultaneous formation of an atom of another element. This theory, which accounts satisfactorily for all the facts of radioactivity, presupposes the complexity of the atom, that is, that it has a structure.

### § 5 The Rutherford-Bohr Atom

The production of identical electrons from varying kinds of matter had revealed the complex nature of the atom and naturally led to attempts to evolve a picture of the structure of the atom. A noteworthy attempt of this kind was that of J. J. Thomson in 1898. It is clear that as the electron has a negative charge, and since the atom is electrically neutral, there must be, somewhere in the atom, a charge of positive electricity exactly equivalent to the charge of the constituent electrons. Thomson supposed that the electrons comprised the whole mass of the atom, and that they were "embedded" in a "sphere of positive electrification."

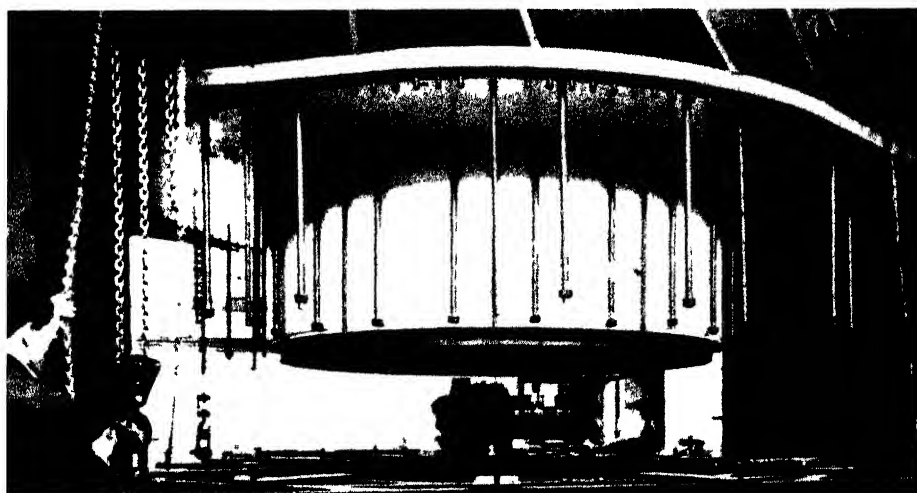
This theory was seen to be untenable when the results of Rutherford's experiments on the tracks of  $\alpha$ -particles in matter and, in particular, in gases became known. A typical diagram of such tracks is given in Plate 1.

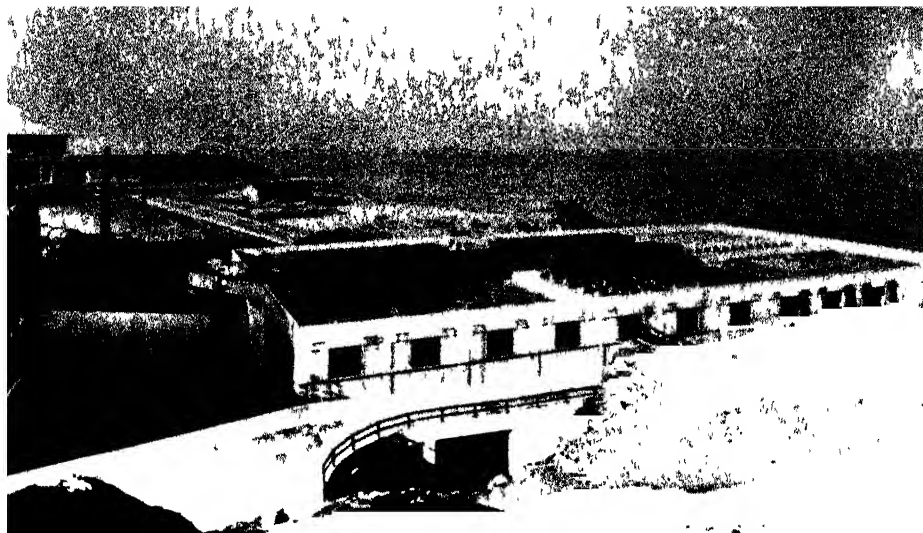
It is thus seen that, in general,  $\alpha$ -particles travel in straight lines without suffering any deflection, but that occasionally an  $\alpha$ -particle is deflected through a very large angle, and at the same time a small spur can be seen, as of something moving in another direction. It is clear that as a rule an  $\alpha$ -particle must pass



1 Track of an alpha-particle

2 Cyclotron at Harwell (see p 167)





3 Bromine from sea water (see p. 557)

4 Magnesia from sea water — general view of plant at Hartlepool



a great many gas molecules without there being any effect on its own track, but that on occasion it is deflected by collision with an atom of gas, the gas atom itself being caused to recoil with considerable velocity. It follows accordingly that the effective mass of the atoms of the gas must be concentrated in a nucleus which is extremely minute, even in comparison with the atom itself as a whole. Further, it is evident that this nucleus carries a large positive charge, since the  $\alpha$ -particle itself is positively charged.

Rutherford was thus led to suggest that the atom consists of an extremely minute nucleus carrying a positive charge, surrounded by electrons, which are perhaps revolving in orbits round this nucleus and which are equal in number to the nuclear positive charge, thus making the atom as a whole electrically neutral. The mass of these electrons being extremely small, virtually the whole mass of the atom is thus concentrated in the nucleus.

As a result of his work on the X-ray spectra of the elements, Moseley (see page 136) suggested that the atomic number, which clearly represents something fundamental in the atom, is in fact equal to the net positive charge on the nucleus. This was confirmed by Chadwick in 1920 by calculations based upon measurements of the scattering of  $\alpha$ -particles passing through thin sheets of metal. He thus obtained values 29.3, 46.3 and 77.4 for the nuclear charge of platinum, silver and copper, which are in good agreement with the values for their atomic numbers as found from their position in the Periodic Table and from Moseley's experiments, viz., 29, 47 and 78.

The atomic number is usually about half the atomic weight. Now hydrogen is the lightest atom known and hence has the lightest nucleus, and it is evident, since only one electron can be removed from the hydrogen atom (for hydrogen can only "take up" one positive charge), that the hydrogen nucleus of mass 1 carries also a positive charge of one unit. This is known as a **proton**. Further evidence in support of the view that the hydrogen atom consists of a nucleus carrying unit positive charge together with one extra-nuclear electron is afforded by Bohr's success in calculating the spectrum of hydrogen on this assumption (page 148).

The diameter of the nucleus is believed to be of the order of  $10^{-13}$  cm. and the effective diameter of the atom as a whole, from the results of X-ray and electron-diffraction experiments, is found to be about  $10^{-8}$  cm. The nuclei of the other elements, if they consisted only of these positively charged units, would have weights approximately *equal* to their atomic numbers, whereas in fact their weights are roughly *twice* the atomic numbers. The difference is accounted for by supposing that the nuclei of the later elements contain electrically neutral particles called **neutrons** each of the same weight as a proton, and equal in number to the difference between the weight and atomic numbers of the nuclei concerned.\* Free neutrons are emitted when some light elements (e.g., beryllium) are bombarded with  $\alpha$ -rays.

Rutherford's conception of the atom is the basis of present-day views of atomic structure; but modifications have been introduced by Bohr, Schrödinger and others, so far as concerns the motions of the orbital electrons, in order to account for the observed phenomena of radiation as revealed in the spectra of the elements; and for the fact that electrons in motion are now found to behave as if they were associated with characteristic waves (see pages 147 and 159). With these modifications this theory is able to correlate many observed phenomena in a very satisfactory way.

\* It was formerly supposed that the nucleus contains electrons, since these are emitted in some radioactive changes. It is now believed that they are formed at the moment of disintegration, with the simultaneous production of a proton, from a neutron. The discovery of a positive particle having the same mass as an electron and termed the positron has also been reported. It has only a transitory existence and, like a number of other particles which have been reported (e.g. the meson, the neutretto and the neutrino), is of comparatively small importance in chemistry.

### § 6 The Position of the Radio-Elements in the Periodic Table. Isotopes

It was natural that when the Disintegration Theory of radioactive change had established itself, investigation should have begun into the chemical nature of the various elements comprising the radioactive series, with a view to their characterization and to the end that they might be assigned to their proper places in the Periodic Table. As this work proceeded two important facts emerged. First, that these various elements are not all chemically distinct either from each other, or, in some cases, from previously known elements, although their radioactive properties are quite distinct; and secondly, that their position in the Periodic Table is closely connected with the nature of the change (whether  $\alpha$ -ray or  $\beta$ -ray) by which they are produced.

At the beginning of 1913, several investigators stated that the expulsion of an  $\alpha$ -particle by a radioactive element causes the residual product to shift its position two "places" in the Periodic Table in the direction of diminishing mass, so that the residual product is not in the next family, but in the next but one. Similarly, when an element gives off a  $\beta$ -particle, the product shifts its position one "place" in a direction opposite to that for an  $\alpha$ -ray change. Hence 'two changes attended by the emission of  $\beta$ -particles, and one by an  $\alpha$ -particle, would bring the product back to its original position in Mendeléeff's table. This is the **displacement rule**: whenever an  $\alpha$ -particle is expelled by a radioactive element, the position in the table to which the resultant product belongs corresponds to an atomic number two units less than that to which the parent belongs; and when an element gives off a  $\beta$ -particle, with or without the accompaniment of X-rays, the resultant product shifts its position so that it becomes that corresponding to an atomic number one unit greater than that to which the parent belongs. This is illustrated for the uranium series by Fig. 10 2. Similar tables have been compiled for the actinium

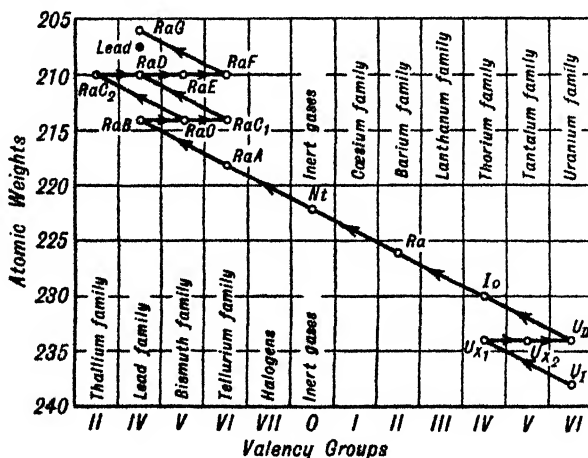


FIG. 10.2.—Arrangement of the Uranium-Radium Family in the Periodic Table

and thorium series. Further, when any number of radioactive elements occupy one place in the Periodic Table, these elements cannot be separated from one another by any known chemical process. Thus, when mesothorium-I gives off two  $\beta$ -particles and one  $\alpha$ -particle to form thorium-X, it is claimed that the two substances cannot be separated from one another chemically in spite of the difference in their atomic weights; and they are probably spectroscopically



indistinguishable. These non-separable elements are what F. Soddy called **isotopic elements**, or **isotopes**, e.g., ionium, thorium, and radio-thorium are isotopes, and mesothorium is isotopic with radium (*vide supra*). The different forms of lead discovered by Soddy connected with radioactivity (1914) are also said to be isotopic, for they have the same atomic volumes and the same chemical properties.

These facts are readily explained by the modern theory of the atom, for as we have seen the chemical properties of an element and its position in the Periodic Table are determined by the net positive charge on the nucleus. It is evident that the expulsion of an  $\alpha$ -particle (a charged atom of helium) will reduce the weight of an atom by four units and the positive charge on the nucleus by two units. Similarly, the loss of an electron (which must, in a radioactive change, be produced from the nucleus) will increase the nuclear charge by one unit without appreciable change in weight.

The discovery of isotopes among the radio-elements, along with the development of the theory of atomic structure which so successfully accounted for them, directed attention to the possibility of the existence of isotopes of the common elements. A very careful series of experiments by Richards (1914) on the atomic weight of lead derived from various sources showed that variations in this value undoubtedly exist; a conclusion which has been confirmed by several later workers. Values as low as 205.927 and as high as 207.9 have been recorded for lead from radioactive minerals; the value for common lead from galena being 207.21.

In the case of the radio-elements, the detection of isotopes is a relatively simple matter, since it depends upon radioactive data: no such method is available for the common elements. The only satisfactory criterion, a method of comparing the masses of *individual* atoms, was, however, in process of development at the time when the possibility of the existence of these isotopes was being discussed. This was J. J. Thomson's parabola method of positive ray analysis. This has been developed by Aston, and by Dempster and Bainbridge, into a very accurate method for the investigation of atomic masses. It depends primarily upon the observation of Goldstein (1886), who noticed that when a perforated cathode is employed in the vacuum tube used for producing cathode rays, luminous rays pass backwards through these perforations. These rays he called canal rays, and it was later shown that they consist of positively charged particles of atomic size. Hence they are now usually known as **positive rays**.

The method consists essentially in subjecting the stream of positively charged particles to the combined action of transverse electric and magnetic fields whereby the particles are made to follow parabolic courses, the size and shape of the parabola followed depending upon the mass of the particles concerned. These parabolas are focused on a photographic plate and from the position of the trace so made the mass of the atoms concerned can be calculated. Measurements of optical spectra can also be applied to the detection of isotopes.

J. J. Thomson's original experiments with apparatus of this kind were made before discoveries in the field of radioactivity had revealed the existence of isotopes, but he had made observations which could not be adequately explained until that later discovery cleared up the matter. In particular, Thomson had noticed, when investigating positive rays from neon, that there was evidence of a particle for which the ratio of the mass to the charge was 22. The suggestion that this was caused by particles of carbon dioxide from the stopcock grease carrying *two* charges, was disproved by cooling the gas with liquid air, which removed the  $\text{CO}_2$  particle with a single charge (44), but left the line at 22 unaffected.

After the existence of isotopes among the radio-elements had been discovered, and lead from different sources had been shown to have different atomic weights, the suggestion was made that Thomson's results were a consequence of the presence of a second isotope in ordinary neon, of atomic weight 22; the gas being in fact a mixture of two or possibly more sorts of atoms of atomic weights 20 and 22, and perhaps others as well. This might be the explanation of the fractional atomic weight of neon (20.18), and similar considerations could be applied to other elements.

The investigation of this problem demanded an apparatus of greater accuracy than Thomson had used, and the subject was taken up by Aston who developed the mass spectrograph, as he termed it, to be capable of a high degree of accuracy.

### § 7 Isotopes of the Non-radioactive Elements. The Mass Spectrograph

A general idea of the construction and use of Aston's mass-spectrograph is given by Fig. 10.3. The radiations are produced by means of an X-ray bulb *B*, of which the anode *A* and perforated cathode *C* are of aluminium. The concentrated stream of electrons from the cathode falls on the silica bulb *D*. This cuts down unwanted X-rays and protects the glass of the bulb. A minute leak allows

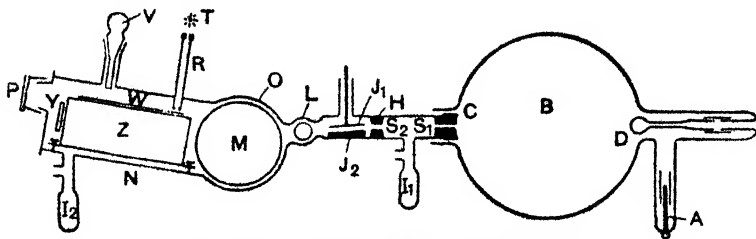


FIG. 10.3. Section of Mass Spectrograph

(From Aston, "Isotopes" by permission of Messrs Edward Arnold and Co., Ltd)

the entry of a trace of the vapour of a suitable volatile compound of the element under examination. Positively charged atoms result by the loss of electrons in the ionizing atmosphere and these pass through the perforated cathode, forming a beam of swift, positive particles. This beam is passed through two very fine slits, *S*<sub>1</sub> and *S*<sub>2</sub>, so forming a ribbon-beam of particles travelling in parallel directions. The particles are then deflected by a powerful electrostatic field maintained by the plates *J*<sub>1</sub>, *J*<sub>2</sub>; it can be shown that this deflection is proportional to  $\frac{e}{mv^2}$  where

$$\begin{aligned} e &= \text{charge on a particle} \\ m &= \text{mass of a particle} \\ \text{and } v &= \text{velocity of a particle.} \end{aligned}$$

After passage, near the stopcock *L*, through a diaphragm not shown, which selects a portion of this deflected beam, the particles are then acted upon by an intense magnetic field (produced by the electromagnet *M*) so arranged as to cause deflection in the same plane, but in the opposite direction. This deflection is proportional to  $\frac{e}{mv}$ , and so it is possible, by careful adjustment of the strengths of the two fields, to bring the "rays" to a focus at a position which then depends only upon  $\frac{e}{m}$  and is independent of the speed. A photographic plate *W* is placed at this focus and so reveals, on development, a series of lines, each of which corresponds to a group of particles all of the same mass (strictly the same ratio  $\frac{e}{m}$ ). This selective deviation of the particles from their original path is very similar to the dispersion of light by a prism. Consequently, the nomenclature of light is adopted: hence "mass spectrograph" and "mass spectrum." This "spectrum" can be calibrated from the positions of the lines due to certain common elements always present, and so the masses of the particles producing the other lines can be calculated.

When it is desired to investigate an element from which no suitable volatile compound is available, a compound is fused on to the anode itself which is then heated electrically.

Several improvements and refinements have been introduced into this apparatus lately whereby its accuracy and precision have been greatly increased, but in fundamentals the method remains the same.

Dempster in America has also developed a mass spectrograph of rather different design in which the intensities of the spots (or lines) can be measured electrically. Bainbridge also has devised an apparatus which gives a linear relationship between the mass of the particle and the position of its line on the plate.

As a result of this work, the great majority of the known elements have been found to have isotopes. Even hydrogen itself has an isotope of mass 2. Eighty-three of the first 92 elements have now been examined; 23 are simple, consisting of atoms of one mass only, the remainder consisting of two or more isotopes. Table XI gives a list of known isotopes apart from the artificially produced trans-uranium elements.

The results summarized in Table XI lead to certain remarkable and interesting conclusions. Thus, in view of the fact that so many elements consist of mixtures of two or more kinds of atoms, it is remarkable that their atomic weights, as determined by the ordinary chemical methods, are so constant. The only elements for which, so far, differences in atomic weight have been detected in different samples are sulphur and lead; lead is known from the study of radioactivity to be derived from two different sources; even meteoric samples have atomic weights indistinguishable from those of their terrestrial counterparts. For the non-radioactive elements we are forced to the conclusion either that since they were formed they have been so thoroughly mixed that the proportions of the various isotopes present has settled down to a fixed ratio which nothing has since succeeded in disturbing, or else that when they were first produced the process producing them did so in fixed proportions.

Another interesting conclusion to be drawn from the above table is that Prout's hypothesis is in a very real sense a true one, although not quite perhaps in the sense that he understood it. It is now clear that the masses of the individual atoms are whole numbers (though for a reason shortly to be discussed—§ 8—not exact multiples of that of a hydrogen atom), and they are built up of units of which the hydrogen nucleus is the chief.

It is curious to note that no odd-numbered element, with the possible exception of potassium and of the isotope of hydrogen of mass 3, has more than two isotopes; whereas the even elements frequently have a great many. The most complex element from this point of view, so far as present information goes, is tin, with ten isotopes, ranging from 112 to 124. Another remarkable fact which emerges is that a stable elementary atom is now known for almost every mass-number up to 210; some places are filled twice over, and a few three times, with *isobares* (atoms of the same weight but different chemical properties).

### § 8 Mass-Spectra and Atomic Weights

Quite soon after Aston had begun the search for isotopes of the non-radioactive elements, it became clear that the atoms comprising a great many elements had a mass very close to whole numbers in terms of oxygen = 16. But even with the first mass spectrograph, whose "resolving power" was comparatively small by the side of the latest apparatus, Aston was able to show that hydrogen is not represented by an exact whole number on this scale. The discrepancy is accounted for by the modern view that mass is electrical in origin, and that when, in the remote past, the nucleus in question was formed from protons and neutrons there was a loss of mass and an enormous amount of energy was liberated equivalent to this loss of mass according to the equation  $E = mc^2$  (cf. page 53). Thus the total mass of this nucleus will not be equal to the combined masses of the protons and neutrons which compose it, but something slightly less than this. The hydrogen nucleus, which contains no neutrons, will thus have a mass slightly greater than, for example, one-sixteenth of that of an oxygen atom (disregarding for the moment the isotopes of oxygen, concerning which see below). This is known as the *packing effect* and Aston has shown that in many cases it differs

TABLE XI.—TABLE OF ISOTOPES

Atomic Number	Element	Atomic Weight	Isotopes (in order of abundance)
1	Hydrogen	1.008	1, 2, 3
2	Helium	4.003	4, (3)
3	Lithium	6.940	7, 6
4	Beryllium	9.013	9
5	Boron	10.82	11, 10
6	Carbon	12.011	12, 13
7	Nitrogen	14.008	14, 15
8	Oxygen	16.0000	16, 18, 17
9	Fluorine	19.00	19
10	Neon	20.183	20, 22, 21
11	Sodium	22.991	23
12	Magnesium	24.32	24, 25, 26
13	Aluminium	26.98	27
14	Silicon	28.09	28, 29, 30
15	Phosphorus	30.975	31
16	Sulphur	32.066	32, 34, 33, 36
17	Chlorine	35.457	35, 37
18	Argon	39.944	40, 36, 38
19	Potassium	39.100	39, 41, 40
20	Calcium	40.08	40, 44, 42, 48, 43, 46
21	Scandium	44.96	45
22	Titanium	47.90	48, 46, 47, 49, 50
23	Vanadium	50.95	51
24	Chromium	52.01	52, 53, 50, 54
25	Manganese	54.94	55
26	Iron	55.85	56, 54, 57, 58
27	Cobalt	58.94	59
28	Nickel	58.71	58, 60, 62, 61, 64
29	Copper	63.54	63, 65
30	Zinc	65.38	64, 66, 68, 67, 70
31	Gallium	69.72	69, 71
32	Germanium	72.60	74, 72, 70, 73, 76
33	Arsenic	74.91	75
34	Selenium	78.96	80, 78, 76, 82, 77, 74
35	Bromine	79.916	79, 81
36	Krypton	83.7	84, 86, 82, 83, 80, 78
37	Rubidium	85.48	85, 87
38	Strontium	87.63	88, 86, 87, 84
39	Yttrium	88.92	89
40	Zirconium	91.22	90, 92, 94, 91, 96
41	Niobium	92.91	93
42	Molybdenum	95.95	98, 96, 95, 92, 94, 97, 100
43	Technetium	—	
44	Ruthenium	101.7	102, 101, 104, 100, 99, 96, 98
45	Rhodium	102.91	103
46	Palladium	106.7	104, 105, 106, 108, 110, 102
47	Silver	107.880	107, 109
48	Cadmium	112.41	114, 112, 110, 111, 113, 116, 106, 108
49	Indium	114.82	115, 113
50	Tin	118.70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115

TABLE XI.—TABLE OF ISOTOPES—*continued*

Atomic Number	Element	Atomic Weight	Isotopes (in order of abundance)
51	Antimony	121.76	121, 123
52	Tellurium	127.61	130, 128, 126, 125, 124, 122, 123, 120
53	Iodine	126.91	127
54	Xenon	131.3	129, 132, 131, 134, 136, 130, 128, 126, 124
55	Caesium	132.91	133
56	Barium	137.36	138, 137, 136, 135, 134, 130, 132
57	Lanthanum	138.92	139, (138)
58	Cerium	140.13	140, 142, 136, 138
59	Praseodymium	140.92	141
60	Neodymium	144.27	142, 144, 146, 143, 145, 148, 150
61	Promethium	—	
62	Samarium	150.35	152, 154, 147, 149, 148, 150, 144
63	Europium	152.0	153, 151
64	Gadolinium	157.26	156, 158, 155, 157, 160, 154, 152
65	Terbium	158.93	159
66	Dysprosium	162.51	164, 162, 163, 161, 160, 158, (156)
67	Holmium	164.94	165
68	Erbium	167.2	166, 168, 167, 170, 164, 162
69	Thulium	169.04	169
70	Ytterbium	173.04	174, 172, 173, 176, 171, 170, 168
71	Lutecium	174.99	175, 176
72	Hafnium	178.50	180, 178, 177, 179, 176, 174
73	Tantalum	180.95	181
74	Tungsten	183.86	184, 186, 182, 183, 180
75	Rhenium	186.22	187, 185
76	Osmium	190.2	192, 190, 189, 188, 186, 187, 184
77	Iridium	192.2	193, 191
78	Platinum	195.09	195, 196, 194, 198, 192
79	Gold	197.2	197
80	Mercury	200.61	202, 200, 199, 201, 198, 204, 196
81	Thallium	204.39	205, 203
82	Lead	207.21	208, 206, 207, 204
83	Bismuth	209.00	209
84	Polonium	—	
85	Astatine	—	
86	Radon (Niton)	222.00	
87	Francium	—	
88	Radium	226.05	
89	Actinium	—	
90	Thorium	232.05	232
91	Protoactinium	231.0	231
92	Uranium	238.07	238, 235, 234

slightly from atom to atom. The magnitude of the divergence of the mass of any given atom from the whole number rule ( $O = 16$ ) is known as the **packing fraction**. These divergencies are, of course, very small, being of the order on the average of  $10^{-4}$ ; the departure of atomic weights, as determined by chemical methods, from whole numbers being due, as has been shown, to the existence of isotopes.

It is clear that if we know the packing fraction of a given element, and the relative abundance of each isotope in the element, as ordinarily prepared, we can calculate the value of the chemical atomic weight. It is only quite recently that it has been practicable to determine either of these quantities with sufficient accuracy for the purpose, but the refinements introduced into the apparatus by Aston, and by Dempster and others, have now enabled this to be done, and the atomic weights of many elements have now been determined by this method. Where the result differed markedly from the accepted chemical value, redetermination of the latter has usually resulted in a change to a value very close to the result obtained from mass-spectrograph data. It is noteworthy that two methods so essentially different in principle should give results so concordant, and it may be concluded that the theories underlying each have a substantial foundation of truth.

The discovery of isotopes has reduced somewhat the importance of atomic weights as physical constants, for it is now seen that the atomic weight is a statistical mean of the weights of the atoms present, and only when the element is simple does it represent the weight of any actual atom. The important constants are now for any individual *atom* its mass number and atomic number, which respectively determine its weight and its chemical (and to a large extent physical) properties. But the remarkable constancy of atomic weights, already referred to, indicates that their importance for ordinary chemical work and calculations, in particular those involved in quantitative analysis, remains unaltered.

In this connection the fact (recorded in Table XI) that oxygen consists of three isotopes has important consequences. The existence of isotopes of oxygen of masses 17 and 18 was not at first detected by the mass spectrograph as the proportions in which they are present are too small to enable them to be identified with certainty by being distinguished from charged particles of  $OH$  and  $OH_2$ , normally present in small quantities. Their presence was revealed by a study of the molecular band spectrum of oxygen, by which means they were shown to be present to the extent of 1 part in 2,500 and 1 part in 500 respectively. The chemical atomic weight of an element, referred to oxygen  $\approx 16$ , will thus differ slightly from the atomic weight calculated from mass spectrograph data alone which is referred to  $O^{16} = 16$  (i.e., the abundant isotope) as standard. This difference is allowed for in comparing the results of the two methods, in the way previously described.

The discovery of a second isotope of hydrogen, of mass number 2, was a consequence of the recognition of the "complex" nature of oxygen (as is described on page 296), since the agreement between the chemical and the mass-spectrograph values for atomic weight of hydrogen was thereby seen to be fortuitous.

## CHAPTER 11

# THE OUTER SPHERE OF THE ATOM.

### VALENCY

Let us learn to dream, then perhaps we shall find the Truth.—A. KEKULE.

#### § 1 The Structure of the Atom and the Spectra of the Elements

RUTHERFORD's initial suggestion as to the structure of the atom postulated the existence of a central, positive nucleus, surrounded by electrons equal in number to the net nuclear charge, thus preserving the electrical neutrality of the atom. If the atom be constituted in some such way as this it is reasonable to suppose that it is the extra-nuclear electrons which are responsible for the chemical properties, since they will be the parts of each atom most readily available for reaction with another atom. It is thus a matter of the first importance to discover the way in which the electrons are arranged in the outer part of the atom since differences between the chemical properties of different elements can reasonably be ascribed to differences of electronic arrangement. Rutherford assumed that these extra-nuclear electrons rotate round the nucleus and thus are kept from falling into the nucleus by their centrifugal force. The difficulty then arises that, on the basis of classical dynamics, such rotating electrons would radiate energy continuously in the form of electromagnetic waves (light, etc.), and this energy being derived from that of the rotating electrons themselves, it would follow that their speed would gradually be reduced and they would eventually fall into the nucleus.

The way out of this difficulty was suggested in 1913 by N. Bohr who applied the principles of the *Quantum Theory* to the problem. For some years previously it had been clear that the principles of ordinary classical dynamics were not applicable to the problems of radiation in general, and in order to account for the observed results, M. Planck put forward the *Quantum Theory of Radiation*. According to this theory the energy of vibration is not radiated or absorbed continuously, but is given out, or taken in, in small, discrete portions called quanta, whose magnitude is not, however, universally constant for all radiations, but is proportional to the frequency of the particular radiation concerned, or, what is in reality the same thing, the frequency of the vibrating system producing the energy radiated. Thus where  $\nu$  is the frequency of vibration the magnitude of the quantum of energy is given by  $h\nu$  where  $h$  is a universal constant known as Planck's constant. Energy can only be radiated from a system whose vibration frequency is  $\nu$  in amounts which are exact, integral multiples of the quantum for this system, that is, exact multiples of  $h\nu$ .

This theory has been very successful in accounting for many physical phenomena which could not be explained on the basis of classical mechanics, and so is regarded as established.

In applying the quantum theory to the problem of atomic structure Bohr made the following assumptions:

- (i) of all the theoretically possible orbits (possible spatially, that is) of an electron rotating round the nucleus, only certain orbits are permissible—all others are forbidden. These orbits are known as *stationary states*;
- (ii) an electron radiates energy *only* when passing from one permissible orbit to another of lower energy;
- (iii) the positions of the permissible orbits are related in that an electron may possess 1, 2, 3 . . .  $n$  quanta of energy according to which of the  $n$  permissible

orbits it is in. Each orbit is characterized by the *quantum number* (later known as the *principal quantum number*)  $n$ . The energy of any given electron is thus given by  $nh\nu$ .

An electron passing from one orbit to the next will radiate (or absorb) one quantum of energy, that is, if  $E_1, E_2$  are the energies of two consecutive stationary states, the energy radiated has a frequency given by  $E_1 - E_2 = h\nu$ .

Bohr achieved a remarkable success with this theory of the atom when he applied it to the calculation of the spectrum of hydrogen. On classical theories, if radiation were emitted from rotating electrons, all frequencies should be represented in the spectrum, which should therefore be continuous. The spectrum of a glowing vapour is in fact a line spectrum, i.e., its radiation comprises a limited number of definite frequencies only. Assuming that hydrogen has a nucleus with one positive charge round which one electron rotates, Bohr was able to calculate the positions of all possible lines in the hydrogen spectrum and his results are in exact agreement with the observed values.

### § 2 The Structure of the Atom and the Periodic Table

Bohr's quantum number,  $n$ , which defined each orbit, conceived of it as circular; clearly elliptical orbits would be possible and to include these Bohr introduced a

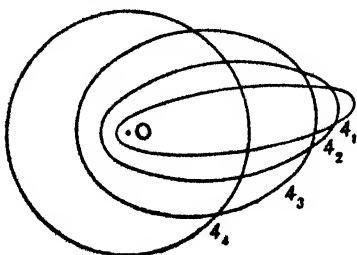


FIG. 11.1 — Bohr Orbits of Quantum Number  $n = 4$

second quantum number written as a subscript to the first. These two quantum numbers were used to describe the state of each electron. (Fig. 11.1 indicates the ideas embodied in the theory of that time.) Bohr's work served to establish beyond doubt the validity of the quantum mechanical treatment of the behaviour of the electrons in the atom. Later developments, by Sommerfeld and others, considerably modified and extended the Bohr Theory, and the newer Quantum Theory of the Atom is based upon a number of postulates which, by making use, principally, of the data provided by the spectra of the elements, have enabled the pattern

of the electronic arrangements of the atoms of all the elements to be discerned with reasonable certainty.

These results are based upon the application of five principles. The condition of each electron is characterized by four quantum numbers known as the principal ( $n$ ), azimuthal ( $l$ ), magnetic ( $m$ ) and spin ( $m_s$  or  $s$ ) quantum numbers respectively. Four principles (which can be proved to be valid by the methods of Quantum Mechanics) define the relationship between these four quantum numbers for any given electron, viz.,

1.  $n$  may be any positive integer from unity upwards;
2.  $l$  may be any integer from zero to  $n - 1$ .  
(so far there is no evidence that any value of ' $l$ ', greater than 3, is involved in atomic structure),
3.  $m_l$  may be any integer from  $+l$  to  $-l$ ;
4.  $m_s$  (or  $s$ ) may be  $+\frac{1}{2}$ , or  $-\frac{1}{2}$ , only.

**Pauli's Exclusion Principle** which states that no two electrons in the same atom can have all four quantum numbers identical is the fifth of the principles referred to above. It is purely empirical with no theoretical basis as yet.

On the basis of these principles it is now possible to determine how the grouping of the electrons changes from element to element of the Periodic Table. It has been concluded that the electrons are located in shells, sometimes denoted by the letters  $K, L, M, N, O, P, Q$  (derived from the nomenclature of X-ray spectra). The Principal Quantum number defines the shell concerned. Thus  $n = 1$  for



*K* shell, 2 for the *L* shell and so on. In defining the state of an electron numerals are used for *n*, values of *l* are represented by the letters *s*, *p*, *d* and *f* where *l* = 0, 1, 2 and 3 respectively. These symbols for *l* are derived from the terms for the spectroscopic series (sharp, principal, diffuse and fundamental) from which they are deduced.\*

It is clear, on the assumption that the outermost electrons are those which are concerned in ordinary chemical processes, that the inert gases must possess an extremely stable structure, which we interpret as meaning that in them the outermost group of electrons is complete and has reached its most stable size. Furthermore, the Periodic Table indicates that we find a reappearance of similar properties after passing 2, 8, 8, 18, 18, and 32 elements respectively. This fact must be reflected in the way in which we assume that the different levels are filled up, as we pass from atom to atom.

The conclusions derived both from physical and from chemical evidence are in good agreement, and have enabled us to assign structures to almost all the elements with a high degree of certainty. These conclusions are embodied in Table XII and may now be considered in slightly greater detail.

In considering the electronic structure of each element in detail it is convenient to assume that we can pass from element to element, adding each time one positive charge to the nucleus, and assigning the consequent additional extra-nuclear electron to its appropriate place in the system. The energy associated with each level in each shell can be calculated and the levels will fill up in order of increasing energy since the level of lowest energy will be the most stable and therefore fill up first. The levels are referred to by the value of *n* and the "letter" value of *l*, e.g., 1*s*, 2*s*, 2*p*, etc. The number of electrons in any given level is indicated by a superscript numeral; thus 2*p*<sup>6</sup> would indicate the presence of six electrons in the 2*p* level (i.e., having principal quantum number 2 and azimuthal quantum number *p*, i.e., one).

#### *First Period of the Periodic Table*

This period contains only hydrogen and helium. The work of Bohr, already referred to, has shown that hydrogen has one electron in a 1*s* orbit, the nucleus being a single proton.

Helium, of atomic weight 4 and atomic number 2, must hence contain 2 protons and 2 neutrons in its nucleus. The extra-nuclear electrons are both in the 1*s* level. This inner pair of electrons in 1*s* orbits is believed to exist in all elements except hydrogen—that it represents a "completed" group is shown by the fact that helium is an inert gas.

#### *Second Period*

The element of atomic number 3 is lithium. Since, according to postulate 2 (page 148), when *n* = 1, *l* can have only one value, zero, it follows that for electrons for which the principal quantum number is one there can be only two sets of values for the four quantum numbers, thus:

<i>n</i>	<i>l</i>	<i>m<sub>l</sub></i>	<i>m<sub>s</sub></i>
1	0	0	$+\frac{1}{2}$
1	0	0	$-\frac{1}{2}$

Applying the Pauli exclusion principle it then follows that there can only be two electrons with principal quantum number, one, in any atom. Hence the third electron in lithium goes into a 2*s* orbit, and since it is situated further from the nucleus, it will be more readily removed than either of the others, and hence we find that lithium is an active element whereas helium is an inert one.

Passing along the first period successive electrons take up orbits represented by principal quantum number 2.

\* The symbol *s* is sometimes used for the spin quantum number and so care is necessary to avoid confusing the two uses.

TABLE XII.—ELECTRONIC

		Number of Electrons in each Sub-shell (or Level)																
		K		L		M			N				O			P		
n =		1	2	3			4				5			6				
l =		s	s	p	s	p	d	s	p	d	f	s	p	d	s	p	d	
Ele- ments	At. No																	
H	1	1																
He	2	2																
Li	3	2	1															
Be	4	2	2															
B	5	2	2	1														
C	6	2	2	2														
N	7	2	2	3														
O	8	2	2	4														
F	9	2	2	5														
Ne	10	2	2	6														
Na	11	2	2	6	1													
Mg	12	2	2	6	2													
Al	13	2	2	6	2	1												
Si	14	2	2	6	2	2												
P	15	2	2	6	2	3												
S	16	2	2	6	2	4												
Cl	17	2	2	6	2	5												
A	18	2	2	6	2	6												
K	19	2	2	6	2	6	1											
Ca	20	2	2	6	2	6	2											
Sc	21	2	2	6	2	6	1	2										
Ti	22	2	2	6	2	6	2	2										
V	23	2	2	6	2	6	3	2										
Cr	24	2	2	6	2	6	5	1										
Mn	25	2	2	6	2	6	5	2										
Fe	26	2	2	6	2	6	6	2										
Co	27	2	2	6	2	6	7	2										
Ni	28	2	2	6	2	6	8	2										
Cu	29	2	2	6	2	6	10	1										
Zn	30	2	2	6	2	6	10	2										
Ga	31	2	2	6	2	6	10	2	1									
Ge	32	2	2	6	2	6	10	2	2									
As	33	2	2	6	2	6	10	2	3									
Se	34	2	2	6	2	6	10	2	4									
Br	35	2	2	6	2	6	10	2	5									
Kr	36	2	2	6	2	6	10	2	6									
Rb	37	2	2	6	2	6	10	2	6			1						
Sr	38	2	2	6	2	6	10	2	6			2						
Y	39	2	2	6	2	6	10	2	6	1		2						
Zr	40	2	2	6	2	6	10	2	6	2		2						
Nb	41	2	2	6	2	6	10	2	6	4		1						
Mo	42	2	2	6	2	6	10	2	6	5		1						
Tc	43	2	2	6	2	6	10	2	6	6		1						
Ru	44	2	2	6	2	6	10	2	6	7		1						
Rh	45	2	2	6	2	6	10	2	6	8		1						
Pd	46	2	2	6	2	6	10	2	6	10								
Ag	47	2	2	6	2	6	10	2	6	10		1						
Cd	48	2	2	6	2	6	10	2	6	10		2						
In	49	2	2	6	2	6	10	2	6	10		2	1					
Sn	50	2	2	6	2	6	10	2	6	10		2	2					

## STRUCTURES OF THE ELEMENTS

		Number of Electrons in each Sub-shell (or Level)																		
		K		L		M			N				O				P			Q
n =		1	2	3			4				5				6			7		
l =		s	s	p	s	p	d	s	p	d	f	s	p	d	f	s	p	d	s	
Ele- ments	At. No																			
Sb	51	2	2	6	2	6	10	2	6	10		2	3							
Te	52	2	2	6	2	6	10	2	6	10		2	4							
I	53	2	2	6	2	6	10	2	6	10		2	5							
Xe	54	2	2	6	2	6	10	2	6	10		2	6							
Cs	55	2	2	6	2	6	10	2	6	10		2	6			1				
Ba	56	2	2	6	2	6	10	2	6	10		2	6			2				
La	57	2	2	6	2	6	10	2	6	10		2	6	1		2				
Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1		2				
Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1		2				
Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1		2				
Pm	61	2	2	6	2	6	10	2	6	10	4	2	6	1		2				
Sm	62	2	2	6	2	6	10	2	6	10	5	2	6	1		2				
Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	1		2				
Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2				
Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1		2				
Dy	66	2	2	6	2	6	10	2	6	10	9	2	6	1		2				
Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1		2				
Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1		2				
Tm	69	2	2	6	2	6	10	2	6	10	12	2	6	1		2				
Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1		2				
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2				
Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2				
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2				
W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2				
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5		2				
Os	76	2	2	6	2	6	10	2	6	10	14	2	6	6		2				
Ir	77	2	2	6	2	6	10	2	6	10	14	2	6	9						
Pt	78	2	2	6	2	6	10	2	6	10	14	2	6	9		1				
Au	79	2	2	6	2	6	10	2	6	10	14	2	6	10						
Hg	80	2	2	6	2	6	10	2	6	10	14	2	6	10		2				
Tl	81	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1			
Pb	82	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2			
Bi	83	2	2	6	2	6	10	2	6	10	14	2	6	10		2	3			
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10		2	4			
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10		2	5			
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1	
Ra	88	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2	
Ac	89	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2	
Th	90	2	2	6	2	6	10	2	6	10	14	2	6	10	1	2	6	1	2	
Pa	91	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	1	2	
U	92	2	2	6	2	6	10	2	6	10	14	2	6	10	3	2	6	1	2	
Np	93	2	2	6	2	6	10	2	6	10	14	2	6	10	4	2	6	1	2	
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10	5	2	6	1	2	
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10	6	2	6	1	2	
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10	7	2	6	1	2	
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10	8	2	6	1	2	
Cf	98	2	2	6	2	6	10	2	6	10	14	2	6	10	9	2	6	1	2	
E	99	2	2	6	2	6	10	2	6	10	14	2	6	10	10	2	6	1	2	
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10	11	2	6	1	2	
Mv	101	2	2	6	2	6	10	2	6	10	14	2	6	10	12	2	6	1	2	
No	102	2	2	6	2	0	16	2	6	10	14	2	6	10	13	2	6	1	2	

Applying the postulates (page 148) the following values are possible for electrons of principal quantum number 2:

$n$	$l$	$m_l$	$m_s$
2	0	0	$+\frac{1}{2}$
2	0	0	$-\frac{1}{2}$
2	1	+1	$+\frac{1}{2}$
2	1	+1	$-\frac{1}{2}$
2	1	0	$+\frac{1}{2}$
2	1	0	$-\frac{1}{2}$
2	1	-1	$+\frac{1}{2}$
2	1	-1	$-\frac{1}{2}$

Pauli's exclusion principle again indicates that there can be only 8 electrons in one atom with principal quantum number 2 and that, of these, only two can have  $l = 0$ , i.e., only two can be  $2s$  electrons, the remainder being  $2p$ . The  $2p$  orbits thus appear first in boron. When the total number of electrons has reached 10 (2 in  $1s$  orbits and 8 in  $2s$  and  $2p$  orbits) we have the inert gas neon. The second quantum group is now complete and the very stable configuration characteristic of an inert gas is produced.

### Third Period

On the addition of an eleventh electron, since the second quantum group is now complete, it passes into a  $3s$  orbit. The resulting system resembles lithium in that we have a solitary electron in the outermost level, with a complete group beneath it, hence the chemical analogy between sodium and lithium. Addition of further electrons, which pass into  $3s$  and  $3p$  orbits ( $3p$  orbits are first found in aluminium), causes the formation of elements which reproduce the general characteristics of the previous period and ends with argon when 8 have been added since neon. We then come once more to an outer group of 8 and the stability of an inert gas appears once more.

### Fourth Period

The first element in this period is potassium, which has one electron in a  $4s$  orbit; the second, calcium, similarly has two electrons in  $4s$  orbits. Thus an analogy exists between these elements and sodium and magnesium respectively. But with the addition of a further electron (i.e., in the element of atomic number 21, scandium) a new phenomenon appears. Scandium does not have three electrons in orbits of principal quantum number 4, but only two, the additional electron passing into a deeper level in the atom by entering a  $3d$  orbit. This process continues as we pass along the fourth period until all possible  $3d$  orbits are filled, the number of  $4s$  electrons remaining unchanged, except in the case of chromium where one of these, too, drops into a  $3d$  orbit, until there are 18 electrons of principal quantum number 3. As soon as this has occurred, the later elements of the period each contain one additional electron for which  $n = 4$  until there are eight of these, when krypton results. We thus see that we have a series of "transition elements" in the middle of this period (cf. Chapter 9, page 126) corresponding to the gradual increase in the number of electrons for which  $n = 3$  from eight to eighteen. These elements show variable valency, form coloured ions, and exhibit other characteristic properties, as well as having the marked "horizontal" relationships characteristic of this portion of the Periodic Table. The later elements of the period, viz., gallium to krypton, resemble the corresponding elements of the third period.

### Fifth Period

This closely resembles the fourth. It begins with two elements having respectively one and two electrons in  $5s$  orbits, after which there follows a series of transition elements, during which the number of  $4d$  electrons increases from eight to eighteen, and ends with a normal series of elements analogous to those in the short periods.

### *Sixth Period*

In this period we find an extension of the phenomenon first observed in the fourth period. The period begins normally with the addition of one and two electrons respectively in  $6s$  orbits, forming caesium and barium respectively. With lanthanum, the next element, the transition group begins, the added electron passing into a  $5d$  orbit, analogous to the corresponding phenomena in the fourth and fifth periods. But the sixth period contains 32 elements, and this expansion in the length of the period is caused by electrons passing into  $4f$  orbits. This process begins with cerium, the fourth element of the period, and continues uninterruptedly until the  $N$  shell has reached thirty-two. This results in the series of rare earths or lanthanous elements which are remarkably alike on account of the fact that the difference from element to element occurs in a deep-down shell of the atom, which is shielded from normal chemical influences by two outer shells of electrons. After passing the rare earths, we have more transition elements corresponding to the filling up of the  $O$  shell, after which the period ends normally.

It is thus to be noted that in the sixth period the group of rare earths is inserted into the transition elements, in the same way, and for an analogous reason, that the transition elements are inserted among the typical elements in the fourth and fifth periods.

### *Seventh Period*

There are but six naturally occurring elements in the seventh period, uranium (At. No. 92) being the last of these, but elements having atomic numbers up to 102 have been produced artificially by the methods indicated in the next chapter (page 168). These are known as *trans-uranic elements*. In the seventh period, after two electrons have gone into the  $7s$  level, the  $6d$  level begins to fill up analogously to the formation of the transition elements of periods four and five, actinium is the first of these. After thorium this process is probably interrupted, in the same way that the formation of the rare earths interrupts the filling up of the  $5d$  levels in the sixth period, and the remaining known elements are analogous to the rare earths in being formed by the successive addition of electrons to the  $5f$  sub-shell. (See also page 760.)

The increase in the number of electrons in the  $N$  shell from 18 to 32 is accompanied by a phenomenon known as the *lanthanide contraction*. The increasing charge on the nucleus, associated with an increase in the number of electrons in a shell deep in the atom, causes the atoms of these elements to contract in comparison with those of earlier periods. This effect is so marked that, for example, the atomic volume of dysprosium is scarcely any larger than that of yttrium in the previous period. Further contraction is observed in the succeeding elements until lutecium (the last of the rare earths) is reached. Hafnium, in which the  $O$  shell begins to expand, has a markedly larger atomic volume.

A consequence of the lanthanide contraction is that there are pairs of elements, such as zirconium and hafnium or molybdenum and tungsten, one occurring before and one after the rare earths, having almost identical atomic volumes.

## § 3 The Structure of the Atoms of the Groups of the Periodic Table

It is instructive to consider in the light of the atomic structures discussed in the previous section, the relations between those assigned to elements falling within the same group or family in the Periodic Table.

The probable structures of the elements in three such groups are given in Tables XIII, XIV and XV which are extracted from Table XII so as to bring together the elements of Groups O, IA, and VIA.

Table XIII gives the structures of the inert gases, and from it we see that these are characterized by having an outer shell to which no more electrons can be added, viz., 8 (except in the case of helium).

In Table XIV, which depicts similarly the configurations of the alkali metals, we find in every case but one electron in the outermost shell, all the inner shells being complete. The outermost electron can be detached forming an ion, which

will be monovalent. (See § 4 for the application of the electronic theory of the atom to valency.) We see that, as in the case of the inert gases, the outermost layer is the same for all the members of the group, and in addition it is seen that the next layer of electrons is also the same.

TABLE XIII.—GROUP O

Electrons $n =$	Number of Electrons in Orbits					
	1	2	3	4	5	6
Helium . .	2					
Neon . .	2	8				
Argon . .	2	8	8			
Krypton . .	2	8	18	8		
Xenon . .	2	8	18	18	8	
Radon . .	2	8	18	32	18	8

TABLE XIV.—GROUP IA

Element $n =$	Number of Electrons in Orbits					
	1	2	3	4	5	6
Lithium .	2	1				
Sodium .	2	8	1			
Potassium .	2	8	8	1		
Rubidium .	2	8	18	8	1	
Caesium .	2	8	18	18	8	1

TABLE XV.—GROUP VIA

Element $n =$	Number of Electrons in Orbits						
	1	2	3	4	5	6	7
Chromium .	2	8	13	1			
Molybdenum .	2	8	18	13	1		
Tungsten .	2	8	18	32	12	2	
Uranium .	2	8	18	32	18	12	2

Table XV gives the structures of a representative group from among the transitional portion of the Periodic Table. In each case these elements have fourteen electrons in the two outermost groups taken together, divided sometimes as 13,1; sometimes as 12,2. The group of thirteen comprises (as may be seen by reference to Table XII) complete groups of eight  $3s$  and  $3p$ , or  $4s$  and  $4p$ , or  $5s$  and  $5p$ , or  $6s$  and  $6p$  orbits, together with an incomplete  $3d$ ,  $4d$ ,  $5d$ , or  $6d$  group as the case may be. The group of twelve is made up similarly. These incomplete groups and the single outer electron are easily removed so that six (or fewer) may be lost, resulting in the considerable variations in valency which we find among the members of this group.

#### § 4 The Electronic Theory of Valency

The conception of valency mentioned briefly in Chapter 7, § 4 (page 100) arose out of the work of Frankland, but, though useful, the idea of valency as a number must, as is now seen, be treated with some caution. The results of modern work

on the nature and structure of the atom have made it possible to elucidate considerably the nature of valency (in the sense of the ability of atoms to combine with one another).

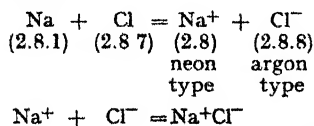
Compounds fall, in general, into one of two classes, viz., electrolytes (that is, substances whose aqueous solutions will conduct electricity—cf. Chapter 15) and non-electrolytes. It is clear that the linking of the atoms which constitutes a non-ionizable valency must differ in some important respect from that involved in an ionizable valency.

Following his discovery of the electron J. J. Thomson, in 1904, suggested that valency might be a consequence of electrostatic attraction caused by the transfer of electrons from one atom to another. Abegg, about the same time, ascribed to each element numerical positive and negative valencies, such that (neglecting signs) their sum is eight, the positive valency being equal to the group number in the Periodic Table. Drude, shortly afterwards, interpreted Abegg's ideas in terms of electrons by suggesting that "Abegg's positive valency number  $v$  signifies the number of loosely attached negative electrons in the atom; his negative valency number  $v'$  means that the atom has the power of removing  $v'$  negative electrons from other atoms or, at least, of attaching them more firmly to itself."

The significance of these observations only became fully apparent after the work of Moseley (page 136) had led to the recognition of the importance of atomic numbers after which, in 1916, two important and independent papers by Kossel and Lewis respectively laid the foundations on which all subsequent theories of valency have been built.

The essential stability and completeness of the 8-electron outer arrangement of the atoms of the Inert Gases (and the 2-electron arrangement in helium) was inherent in the ideas of both Kossel and Lewis. Kossel pointed out that the elements just before the Inert Gases in the Periodic Table form very strongly electronegative ions while those which immediately follow the Inert Gases give rise to highly electropositive ions. Thus chlorine immediately precedes the Inert Gas argon and potassium is the next element after argon. Kossel suggested that such elements gain or lose an electron so achieving the electronic configuration of the nearest Inert Gas with the consequent formation of singly charged monovalent ions. These ions he supposed to combine with each other in the solid compound, on account of the electrostatic attraction between them. Combination in this type of compound is said to involve *electrovalent links* or *electrovalencies*.

Thus, for example, sodium can readily lose one electron to form an ion with an electron grouping similar to that of neon, but, of course, carrying one positive charge. Magnesium similarly can form an ion with two positive charges (Fig. 11.2). In a corresponding manner, at the other end of the period, chlorine by gaining one electron would complete its outer group of 8, thus attaining to a structure comparable to that of argon, and forming an ion carrying one negative charge. In solid sodium chloride the ions are held together by the electrostatic attraction brought about by their being oppositely, but equally, charged. When, however, the solid is placed in a solvent such as water, the electrostatic forces are reduced owing to the high dielectric constant of the liquid and consequently the ions separate and the salt dissolves. The process of combination is thus visualized as indicated in the following scheme:



This theory is in accord with the known facts concerning the behaviour of electrolytes, and the relation between the valency of ions (equal to their charges) and the position in the Periodic Table of the element forming them, as explained in Chapter 15. It is also in harmony with our knowledge of the crystal structure of polar (i.e., ionizable) compounds. (See Chapter 13.)

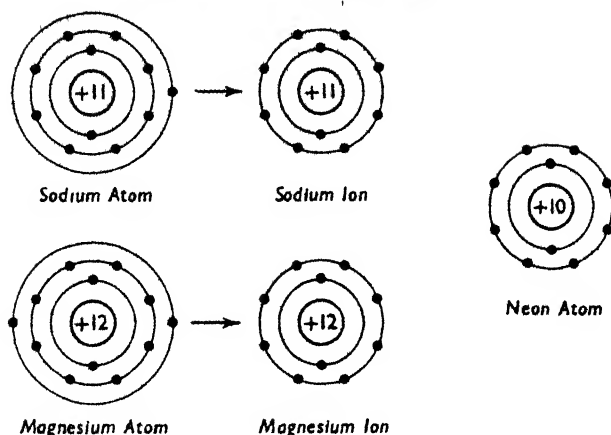
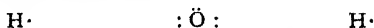


FIG. 11.2.—Structures of Atoms and Ions (diagrammatic)

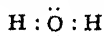
*Covalent Linkages*

The theory outlined above is clearly inapplicable to compounds such as carbon tetrachloride,  $\text{CCl}_4$ , which is a non-electrolyte, or to the molecules of the elementary gases like chlorine in which both of the combining atoms are the same. There is no reason why one chlorine atom should lose one electron in favour of the other nor would the process bring about the stable inert-gas configuration for both atoms. In general, this type of difficulty is experienced when attempting to deal with non-ionizable compounds, which are the great majority, since almost all carbon compounds fall in this category and they alone are more numerous than the compounds of all the other elements together.

G. N. Lewis propounded a theory in 1916 which obviates this difficulty. He, like Kossel, assumes that combination occurs in such a way that the inert-gas configuration is achieved, that being the stable state. The additional assumption which enabled Lewis to explain the formation of non-ionizable (or as they are now known, *covalent*) compounds is the idea that such a link is formed by the *sharing of a pair* of electrons, this pair being able to contribute towards the stability of both the combining atoms. Thus, for example, atoms of oxygen and hydrogen may be indicated thus:



(it is often convenient to represent linkages diagrammatically by showing the outer electrons only). On Lewis's assumption water is formed by the sharing of a pair of electrons by each hydrogen atom, with the oxygen atom, thus completing the stable group of eight (or octet) around the latter and the stable group of two (helium type) around the former. Water is hence represented:



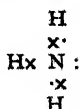
In a similar way chlorine molecule is formed by the sharing of a *pair* of electrons between the two atoms; thus each atom will be associated, in this sense, with eight electrons although there are only fourteen altogether.



Or again, one atom of nitrogen has five electrons in the outer shell. In combining with three atoms of hydrogen to form a molecule of ammonia it shares three of these with the hydrogen along with the three contributed by the hydrogen



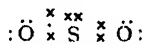
atoms themselves, thus completing its octet. This can be understood from the following formula where the electrons originally belonging to hydrogen atoms are represented by a (x) and those of the nitrogen atom by a dot (·). Thus:



Again, while the nitrogen has achieved the octet of electrons, thus making it conform to the neon type, the hydrogen has similarly and simultaneously attained to the helium type.

#### Co-ordinate Linkages

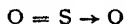
We have seen that according to Lewis's theory a non-ionizable linkage is brought about by the sharing of a pair of electrons, one being contributed in general, by each of the linking atoms. It is possible, however, for a covalent link to be established even when both of the shared electrons are contributed by only one of the atoms. To this type of linkage the term *co-ordinate link*\* has been given, and it may be exemplified by the combination of sulphur and oxygen. The atom supplying the pair of electrons is called the *donor*, the other being known as the *acceptor*. Thus, the atoms of sulphur and oxygen have each six electrons in the outer rings so that if the sulphur atom shares a pair of electrons with one oxygen atom, and donates a pair to another oxygen atom, a molecule of sulphur dioxide is formed, in which each atom has a completed octet. Let the electrons of oxygen be represented by ·, and those of sulphur by x, then the electronic structure can be represented by



Sulphur Dioxide,  $\text{SO}_2$

It must be noted that, once formed, this type of bond is essentially the same as an ordinary covalent link; the only difference is in the source of the electrons comprising the link.

The molecule formed as a result of the sharing of two electrons both derived from one atom in this way will exhibit a certain polarity,† for the sharing will cause the "donor" atom to become somewhat positive and the "acceptor" similarly will be negative. Accordingly this type of linkage is usually symbolized by  $\rightarrow$  instead of by  $-$ . The arrow implies the presence of two electrons, and the head of the arrow is arranged to point away from the donor to the acceptor. Thus, sulphur dioxide has two covalent linkages,  $\equiv$ , and one co-ordinate linkage.



Sulphur Dioxide,  $\text{SO}_2$

Further deductions from, and applications of, this theory, of great importance, are possible but cannot be fully discussed here. Its application to the Werner compounds is considered in Chapter 39.

\* The co-ordinate link is sometimes referred to by other names, e.g., *semi-polar double bond*, *donative bond*, *co-ionic link*.

† A molecule exhibiting polarity of this kind is said to have a *dipole moment*. This quantity, though small (of the order of  $10^{-18}$  electrostatic units), is measurable, and its measurement can be used to demonstrate the existence of co-ordinate links in the molecules of particular compounds.

### § 5 The Spin Quantum Number. Pairing of Electrons

Thus far, in discussing the arrangement of the extra-nuclear electrons in the atom and in applying the results of this discussion to the explanation of the phenomena of valency, only the principal and azimuthal quantum numbers have been considered. A further empirical rule, which has experimental support, is known as the **Rule of Maximum Multiplicity** (sometimes called the **Hund Rule**) and states that "the distribution of electrons in a free atom between the three *p*, five *d*, or seven *f* orbits is such that as many of the orbits as possible are occupied by a single electron before any pairing of electrons takes place." A single electron in any sub-level is said to be *unpaired*; two electrons in any level having all quantum numbers, *except* the spin quantum number, the same are called *paired* electrons.

If the spin quantum numbers be indicated by means of arrows the electronic arrangements of the first ten elements can be represented as follows (the sub-division of the *p* orbits according to the three possible values of the magnetic quantum number being indicated by  $p_x$ ,  $p_y$  and  $p_z$ ):

Element	At. No.	1s	2s	2p <sub>x</sub>	2p <sub>y</sub>	2p <sub>z</sub>
H	1	↓				
He	2	↓ ↑				
Li	3	↓ ↑	↓			
Be	4	↓ ↑	↓ ↑			
B	5	↓ ↑	↓ ↑	↓		
C	6	↓ ↑	↓ ↑	↓	↓	
N	7	↓ ↑	↓ ↑	↓	↓	↓
O	8	↓ ↑	↓ ↑	↓ ↑	↓	↓
F	9	↓ ↑	↓ ↑	↓ ↑	↓ ↑	↓
Ne	10	↓ ↑	↓ ↑	↓ ↑	↓ ↑	↓ ↑

Lewis's Theory attached great importance to a pair of electrons as forming a covalent bond but it was not until the development of Quantum Mechanics that the reason for its importance became apparent. As a result of the application of Quantum Mechanics to the problem it is now believed that a pair of electrons can form a bond only when they have opposite spin (i.e. different spin quantum numbers but the other three quantum numbers the same). The significance of the unpaired electrons in the atom of an element is now clear for covalent bond formation can only occur when an unpaired electron is available.

The number of unpaired electrons in the atoms of each of the elements from hydrogen to neon and the numerical valencies of these atoms are

Element	H	He	Li	Be	B	C	N	O	F	Ne
Unpaired electrons	1	0	1	0	1	2	3	2	1	0
Valency	1	0	1	2	3	4	3	2	1	0

For seven of these elements these two quantities are the same; for beryllium, boron and carbon the former is smaller than the latter. To account for the valencies of these three elements it is necessary to assume that one or more of the paired electrons can be unpaired in compound formation. For this to happen energy must be supplied; the necessary energy is available from the heat evolved when reaction takes place.

With helium no such uncoupling can occur because it would require (by the Exclusion Principle) that one electron should be promoted to a  $2s$  orbit, which corresponds to a large increase of energy whereas, in beryllium or carbon, unpairing can be achieved by one of the electrons in a  $2s$  orbit going to a  $2p$  orbit which involves a much smaller addition of energy. Similar considerations explain the inert character of neon.

### § 6 Electronegativity

The term electronegativity is used to describe the power of an atom to attract an electron. It has been interpreted quantitatively by Pauling and expressed numerically by him. Table XVI gives the values, calculated by Pauling from bond-energy (page 239) and thermochemical data, for a number of elements.

TABLE XVI.—ELECTRONEGATIVITIES

Element	Electronegativity	Element	Electronegativity
Fluorine	4.0	Tin	1.7
Oxygen	3.5	Titanium	1.6
Chlorine	3.0	Zirconium	1.6
Nitrogen	3.0	Aluminium	1.5
Bromine	2.8	Beryllium	1.5
Sulphur	2.5	Scandium	1.3
Carbon	2.5	Yttrium	1.3
Iodine	2.4	Magnesium	1.2
Selenium	2.4	Calcium	1.0
Tellurium	2.1	Lithium	1.0
Phosphorus	2.1	Strontium	1.0
Hydrogen	2.1	Sodium	0.9
Arsenic	2.0	Barium	0.9
Boron	2.0	Potassium	0.8
Silicon	1.8	Rubidium	0.8
Antimony	1.8	Caesium	0.7
Germanium	1.7		

Since the electronegativity of an element indicates the facility with which it gains, or loses, electrons, it describes the way in which it enters into combination with other elements. Thus, elements of high electronegativity have a great tendency to attract electrons and so to form anions and, conversely, elements of low electronegativity can easily form cations. Further, compounds formed between elements whose electronegativities differ most will be the most electrovalent in character and vice versa.

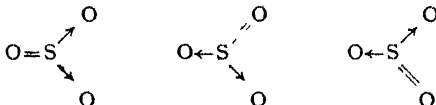
### § 7 Wave Mechanics. Resonance

Reference has been made already (page 139) to modifications, suggested by Schrödinger and others, of the Rutherford theory of atomic structure as developed by Bohr. Their ideas do not invalidate the explanation of the structure of the Periodic Table given above, nor the main lines of the electronic theory of valency, but they have a bearing on our ideas of the constitution of some compounds such as the hydrides of boron (page 736).

Electrons in motion behave as though they are associated with characteristic waves. For example, when reflected from a crystal or passed through thin sheets of metal foil diffraction effects are observed as with X-rays (pages 136, 137), and it is to take account of such facts as these that these changes have been suggested. According to Schrödinger the charge of an electron is not concentrated at a point on a particle but extends into space as a sort of cloud, the density of which is denoted by  $\psi^2$ , where  $\psi$  is known as the wave function and replaces Bohr's electron orbit. The analysis involved in this theory is known as **Wave Mechanics**.

An important consequence of these ideas is the modern theory of **Resonance** which makes it possible to account for the fact that some compounds appear to exist in a state which cannot be precisely formulated but which corresponds to a condition intermediate between those represented by two or more ordinary electronic formulae. This it does by showing that a molecule existing in such an intermediate state would have a lower potential energy than it would have in either of the precisely formulatable conditions, and so would be more stable.

The actual structure of the molecules of the compound concerned is, in such a case, intermediate between that of possible structures which can be formulated; in a sample of the substance all the molecules present are exactly alike. The sample does not consist of a mixture of molecules having different structures. The actual condition of the molecule cannot usually be indicated by a single diagram or formula. Thus, for example, sulphur trioxide can be written in three ways



Experiments have shown that in the sulphur trioxide molecule all three oxygen atoms are exactly similarly situated and bound to the sulphur atom in exactly the same way. This cannot be indicated in a single diagram or formula, it is expressed by saying that sulphur trioxide is a resonance hybrid between these three structures. Examples of other compounds which are otherwise difficult or impossible to account for are nitrous oxide and nitric oxide (pages 459, 463).

### § 8 The Atomic Theory in the Light of Modern Developments

It is natural that the facts and theories discussed in the present chapter should cause us to pause and consider their effect on our conceptions of the atom, of an element and of the atomic theory in general as discussed in previous chapters.

As regards the fundamental postulate that all matter consists of atoms, we now have direct evidence for the truth of this, which was previously only an assumption. But we now know that the atoms of a given element are not necessarily all exactly alike in weight, nor is the atom the indivisible unit that it was formerly supposed to be.

As regards these two latter points, it has been said earlier (page 143) that with the exception of lead from radioactive sources, the elements as we find them show a remarkable constancy in the proportions of the isotopes present, so that the *atomic weight* retains all its former significance in the field of *practical chemistry*. Thus, it is of the highest importance in quantitative analysis. Furthermore, although the hypothesis that the atom of an element is an intricate bit of mechanism, a complex aggregate of parts liable to disruption when exposed to the right conditions, is now generally accepted, this does not affect the time-honoured definition of an atom. **The atom still remains a veritable unit indivisible in chemical transformation.** The facts, speculations, and theories discussed in this chapter do not alter our mode of presenting the facts of material chemistry.

## CHAPTER 12

# NUCLEAR CHEMISTRY

Contending with the fretful elements;  
Bids the wind blow the earth into the sea,  
Or swell the curled waters 'bove the main.—SHAKESPEARE.

### § 1 The Function of the Nucleus in Chemistry

THE theory, developed in the last two chapters, that an atom consists of a positively charged nucleus associated with extra-nuclear electrons, in number equal to the magnitude of the positive charge on the nucleus, leads to the view that it is these extra-nuclear electrons which are responsible for the ordinary chemical properties of these substances. Consequently, in Chapter 11, attention has been directed, largely, to the arrangement and behaviour of these electrons. The effect of the nucleus, apart from the fact that the mass of the atom is almost entirely concentrated in it, on chemical behaviour is exerted through its influence on the number, and hence the arrangement, of the electrons present. It may be argued, therefore, that discussion of the nucleus belongs more properly to the domain of physics rather than that of chemistry but, since changes in the nucleus of an atom must necessarily be accompanied by changes in chemical behaviour, and also because of the increasing interpenetration of physics and chemistry, the study of nuclear transformations is a proper field of inquiry for the chemist.

Nuclear changes can and do occur; some of these take place spontaneously, as in the phenomena of radioactivity, some can be brought about experimentally in the laboratory. These changes can be classified as (i) natural radioactivity; (ii) changes caused by the bombardment of nuclei; (iii) nuclear fission and (iv) nuclear fusion.

### § 2 Radioactivity

A brief outline of the discovery and elucidation of the phenomena of radioactivity has been given in Chapter 10 (page 137). Radioactivity is now seen to be a property of the nucleus and to be a consequence of the inherent instability of some nuclei. Thus, the nuclei of the atoms of all naturally occurring elements whose atomic numbers are greater than 82 (except  ${}_{82}^{208}\text{Pb}$ )\* are unstable and therefore undergo slow decay. These elements are said to be *radioactive*, to exhibit *radioactivity* and to undergo *radioactive disintegration* or *decay*.

\* In the notation used for indicating the nature of nuclei the subscript denotes the atomic number, and the superscript the mass number, of the particular nucleus concerned.

The theory of Atomic Disintegration is now well established as the explanation of these phenomena, and since the breakdown of a radioactive element of high atomic number will result in the formation of another radioactive element, there will be chains of successive elements since the disruption of each one can lead to further breakdown until a stable element is reached. Investigation has shown that there are, among the naturally occurring elements, three such series of radioactive changes known respectively as the uranium, thorium and actinium series. (The last-named is now often referred to as the actinouranium series since actinium, a then new element separated from the residues of pitchblende in 1899, by Debierne, and which is preceded in the series by another "new" element protoactinium, is now known to begin with an isotope of uranium,  ${}^{231}_{88}\text{U}$ .)

The intensity of the activity of the various radio-elements varies very widely so that, for example, whereas a few seconds' exposure to radium is sufficient to fog a photographic plate, several weeks would be necessary for uranium or thorium to produce a similar effect. These differing activities are associated with the differing rates at which the various nuclear species decay and it was shown by Rutherford that the **Law of Radioactive Decay** is that the fraction of the total number of atoms present which undergo disintegration in unit time is constant or, otherwise expressed, the activity diminishes exponentially with the time.

This Law may be expressed mathematically as follows. Let  $N_0$  be the number of atoms present at the beginning and let  $N_t$  be the number which remain after time  $t$ ; then

$$N_t = N_0 e^{-\lambda t}$$

$$\text{or} \quad \lambda = \frac{1}{t} \log_e \frac{N_0}{N_t}$$

where  $\lambda$  is a constant characteristic of each element, being a measure of the relative number of atoms which have disintegrated in unit time. It is usually referred to as the **Decay Constant** or **Radiation Constant**.

It is now usual to characterize the radioactive nuclei by the **half-life period**, i.e., the period after which half the atoms originally present will have disintegrated. Mathematically this may be deduced from the preceding expression since  $N_t$  is now  $N_0/2$  so that

$$\frac{N_0}{N} = 2$$

$$\text{and } \lambda = \frac{1}{t_{\frac{1}{2}}} \log_e 2 \text{ (where } t_{\frac{1}{2}} = \text{the half-life period).}$$

$$\text{Hence } t_{\frac{1}{2}} = \frac{\log_e 2}{\lambda} = \frac{0.693}{\lambda}$$

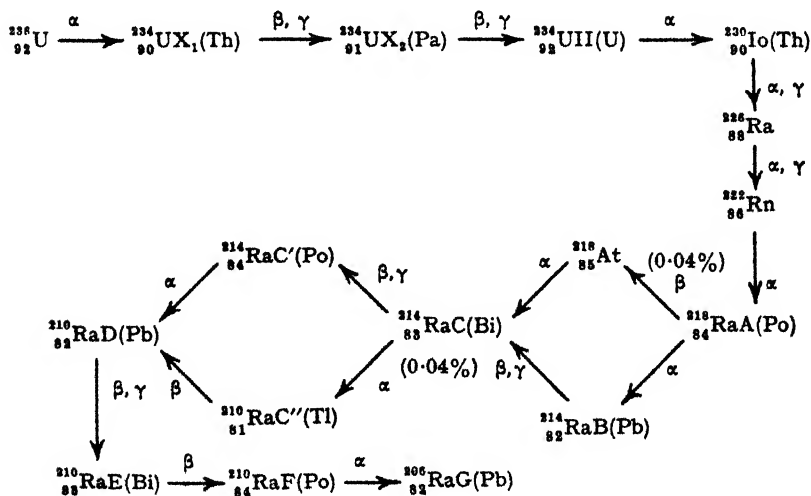
When a radioactive element is undergoing disintegration and thereby giving rise to another radioactive element which decays in its turn to

give further radioactive elements the system will, if not disturbed, ultimately reach a condition in which, for any given element, the same number of atoms will break down in a given time as are being formed in the same time. This condition is described as one of *Radioactive equilibrium* and the total activity will then be constant.

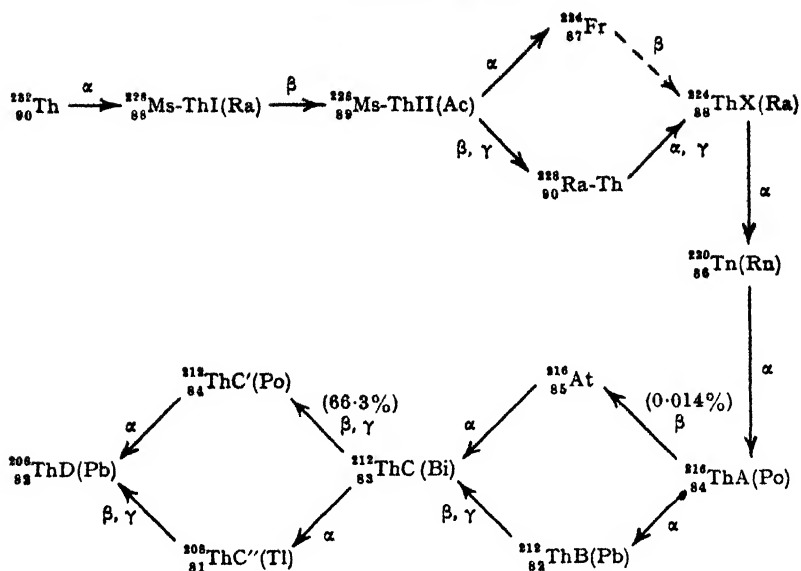
The stages in the disintegration of the three radioactive series are given below and there follows a table giving the half-life periods for all the elements concerned. The nature of the radiation accompanying each change is also indicated. (Changes which have not yet been established conclusively are indicated by dotted lines. The symbols of the common elements are given in brackets.) The end product of all these series is an isotope of lead (atomic number 82). A fourth series, known as the neptunium series, is now distinguished as a consequence of the artificial production of the post-uranium elements. This will be discussed later (page 167) in connection with the description of the processes for the production of these elements.

Changes in the mass of nuclei can take place during  $\alpha$ -ray changes and so occur only in stages of four units. Consequently the mass numbers of all the nuclei in a given series can be represented by a simple mathematical expression. The mass number of thorium is 232, which is divisible by 4, so that the mass numbers of all its disintegration products can be represented by the expression  $4n$  and the thorium series is, therefore, sometimes referred to as the  $4n$  series. The uranium series, similarly, becomes the  $4n + 2$  series and the  $4n + 3$  series is the actinium series. The artificial, neptunium series becomes the  $4n + 1$ , and thus all possible variations in mass numbers are now represented.

### The Uranium Series



## The Thorium Series



## The Actinium Series

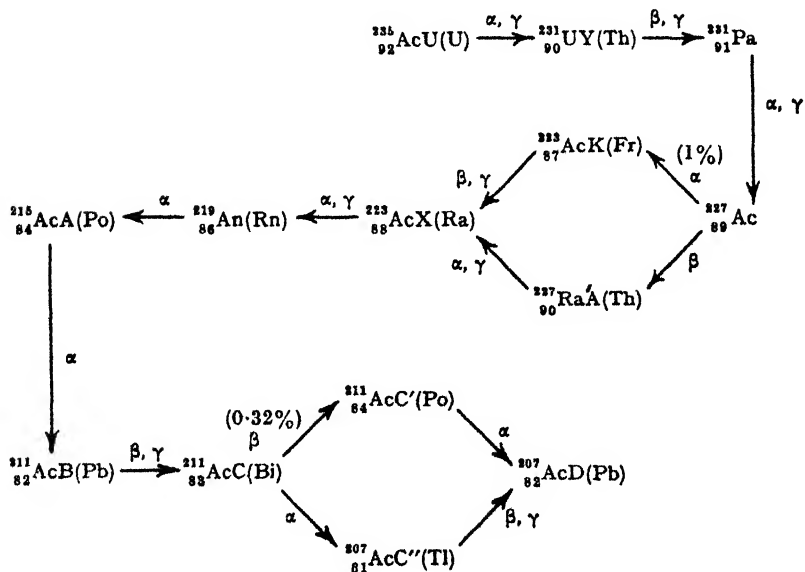




TABLE XVII.—HALF-LIFE PERIODS OF RADIO ELEMENTS

Element	Symbol	Half-life Period	Mass Number
Uranium . . . .	U	$4.498 \times 10^9$ years	238
Uranium $X_1$ . . . .	UX <sub>1</sub>	24.5 days	234
Uranium $X_2$ . . . .	UX <sub>2</sub>	1.14 mins.	234
Uranium II . . . .	UII	$2.67 \times 10^5$ years	234
Ionium . . . . .	Io	$8.3 \times 10^4$ years	230
Radium . . . . .	Ra	1,590 years	226
Radon . . . . .	Rn	3.82 days	222
Radium A . . . . .	RaA	3.05 mins	218
Radium B . . . . .	RaB	26.8 mins.	214
Astatine 218 . . . .	At	a few seconds	218
Radium C . . . . .	RaC	19.7 mins.	214
Radium C' . . . . .	RaC'	$1.47 \times 10^{-4}$ secs.	214
Radium C" . . . . .	RaC"	1.32 mins.	210
Radium D . . . . .	RaD	22 years	210
Radium E . . . . .	RaE	4.85 days	210
Radium F (Polonium)	Po	138.3 days	210
<hr/>			
Thorium . . . . .	Th	$1.39 \times 10^{10}$ years	232
Mesothorium I . . . .	MsThI	6.7 years	228
Mesothorium II . . . .	MsThII	6.13 hours	228
Francium . . . . .	Fr	?	224
Radio-thorium . . . .	RaTh	1.9 years	228
Thorium X . . . . .	ThX	3.64 days	224
Thoron . . . . .	Tn	54.5 secs.	220
Thorium A . . . . .	ThA	$1.58 \times 10^{-1}$ secs.	216
Astatine 216 . . . . .	At	$3 \times 10^{-4}$ secs.	216
Thorium B . . . . .	ThB	10.6 hours	212
Thorium C . . . . .	ThC	60.5 mins.	212
Thorium C' . . . . .	ThC'	$3 \times 10^{-7}$ secs.	212
Thorium C" . . . . .	ThC"	3.1 mins.	208
<hr/>			
Actino-uranium . . . .	AcU	$7.07 \times 10^8$ years	235
Uranium Y . . . . .	UY	24.6 hours	231
Protoactinium . . . .	Pa	$3.2 \times 10^4$ years	231
Actinium . . . . .	Ac	13.5 years	227
Actinium K . . . . .	AcK	21 mins.	223
Radio-actinium . . . .	Ra-Ac	18.9 days	227
Actinium X . . . . .	AcX	11.2 days	223
Actinon . . . . .	An	3.92 secs.	219
Actinium A . . . . .	AcA	$1.83 \times 10^{-3}$ secs.	215
Actinium B . . . . .	AcB	36.1 mins.	211
Actinium C . . . . .	AcC	2.16 mins.	211
Actinium C' . . . . .	AcC'	$5 \times 10^{-3}$ secs.	211
Actinium C" . . . . .	AcC"	4.76 mins.	207

### Applications of Natural Radioactivity

The radioactivity of some naturally occurring elements has been put to practical use, for example, in medicine in the treatment of cancer and other malignant growths, for the manufacture of luminous enamels and as one means of calculating the age of the earth.

Radium and Radon are the radio elements usually used for the treatment of cancerous growths. The radiations from these elements are capable of destroying the cells of the cancerous tissue but they can destroy healthy tissue also (this is particularly true of  $\gamma$ -rays), so that it is necessary to protect the healthy areas, when radium treatment is in progress, by means of shields of lead.

Luminous enamels for the dials of watches and clocks and the instruments of aircraft are made from a mixture of zinc sulphide (which fluoresces when exposed to the radiations of radioactive substances) and a minute quantity of a radium salt. Recently, increasing knowledge about the biological effects of radiation has led to a more cautious attitude to the wearing of watches with luminous dials than was formerly the case, particularly now that the general level of radiation on the earth is tending to be raised by the testing of nuclear bombs and similar devices (compare pages 171 and 176).

The fact that the end product of natural radioactive decay is lead, and that all natural uranium minerals therefore contain lead, furnishes a means for calculating the age of the earth. For this purpose a determination is made of the weight of lead in a known weight of the mineral from which the weight of uranium which has disintegrated in order to yield this weight of lead can be calculated. From this figure and the weight of uranium still present the fraction of the uranium originally present which has decayed into lead can be evaluated and hence, knowing that the half-life period of uranium is  $4.5 \times 10^9$  years, the length of time required for this fraction to decay can be found. Assuming that the pure uranium was deposited when the mineral was first formed this is the age of the earth. This age is found, in this way, to be  $4.6 \times 10^9$  years.

### § 3 Transmutation by Nuclear Bombardment

The transmutation of the elements, in particular of base metals into gold, fascinated mankind for many centuries and the desire to achieve this was the main driving force behind the operations of the alchemists. We now know that, in the changes undergone by the radio elements, transmutation is taking place naturally but no method has so far been discovered for altering, in the slightest degree, the rate at which these changes are going on. In recent years, however, it has been found possible to bring about transmutation of other elements by artificial means, albeit often in only minute quantity. The first way in which this was successfully accomplished was by the bombardment of atomic nuclei by means of other nuclear-sized particles. The first experiments were carried out with  $\alpha$ -particles which were then the only particles available which could be obtained travelling at a sufficiently high speed. Thus, Rutherford, in 1920, bombarded nitrogen atoms with the  $\alpha$ -particles from Radium C and was able to show that hydrogen and an isotope of oxygen had been formed; a change which can be represented by the equation



Since that time means have been developed, such as by the use of the cyclotron and the van de Graaf generator, for accelerating artificially protons, deuterons (the nuclei of the heavy isotope of hydrogen—page 296) and other particles to extremely high speeds and these have enlarged greatly the scope of these experiments. The discovery of the neutron provided a particularly valuable tool since, being uncharged, it can approach the nuclei of atoms without experiencing the intense repulsions which positively charged particles do, and it is thus peculiarly effective.

The principle of the cyclotron may be understood by reference to the diagram (Fig. 12.1). In this instrument, positive particles travelling

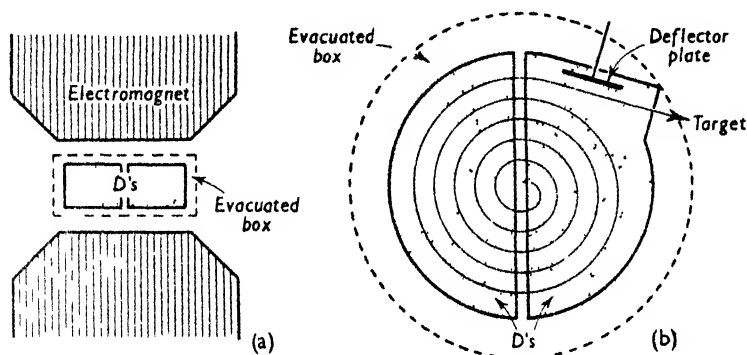


FIG 12—Cyclotron (diagrammatic)

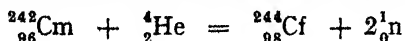
(From Riley, "Principles of the Acceleration of Charged Particles to High Energies," "School Science Review," November 1953)

under the influence of a powerful magnetic field in a path which, in this field alone, would be circular are acted upon also by a series of periodic impulses by means of an extra-high frequency alternating current of approximately 12 million cycles per second. This accelerates the particles and causes them to travel in a spiral path and to reach very high speeds.

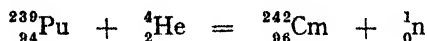
A similar device, which uses the effect on moving electrons of a changing magnetic field, is called the betatron and can accelerate electrons almost to the speed of light. The synchrotron, which uses the same principle with the addition of a series of high-frequency impulses as well as the magnetic flux is being applied to both positive and negative particles.

In artificial transmutations brought about by bombardment the bombarding particle is captured and another particle is emitted. The equations which follow indicate the course of some typical nuclear reactions. The original experiment of Rutherford, mentioned above,

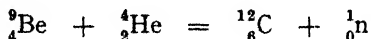
furnishes an example of  $\alpha$ -particle bombardment; another is indicated by



This is an example of the artificial production of a trans-uranium element, californium; curium, the starting point of this equation, is also a trans-uranium element produced artificially according to the equation



The reaction



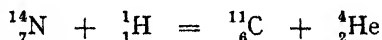
is historically important since it was the reaction in which the neutron was discovered (Chadwick, 1932).

The equation



represents neutron bombardment and capture and is important since the isotope of carbon so formed is radioactive and is being extensively used as a tracer element for following the course of organic reactions and for other purposes (see below, page 174).

An example of proton bombardment is



an  $\alpha$ -particle being emitted. A similar reaction using the nuclei of heavy hydrogen (deuterons) is



It must be noted that energy changes are associated with these transformations in somewhat the same way as with ordinary chemical reactions (cf. Chapter 16) but the quantities involved in nuclear transmutations are extremely large. The heat changes in chemical reactions do not usually exceed 200 Cals. per gram molecule (cf. page 235) at most and are often less than this but in transmutations energies of the order of  $10^6$  Cals. per gram atom are common. These extremely high energy changes result from the interconversion of matter and energy according to the Einstein equation (pages 61, 63). This release of energy is particularly high when nuclear fission (discussed in the next section) occurs.

#### § 4 Nuclear Fission

Before 1938 all the nuclear reactions known were of the same fundamental type, in the sense that the particle initiating the change (e.g., a neutron, a proton or an  $\alpha$ -particle) and one of the products of the reaction, were alike small having a mass of 4 units or less. In 1938, Hahn and Meitner discovered a new type of disintegration. They found that the bombardment of uranium with neutrons caused the uranium

atom to split in such a way that two new atoms of approximately equal mass resulted while the change was accompanied by the release of a (relatively) very large amount of energy. To this phenomenon the term *nuclear fission* has been applied.

In 1934 Fermi had begun to investigate the effect of bombarding uranium with neutrons, arguing that since this particle has no charge it can penetrate the nucleus of another atom much more readily than an  $\alpha$ -particle or a proton. Fermi interpreted the results of these experiments as indicating the production of two new radioactive elements believed to have atomic numbers 93 and 94 and hence to be the first of the trans-uranium elements to be discovered. It is now believed, however, that the effects observed by Fermi were not caused by trans-uranium elements at all but by fission products.

Later work, following up the initial observations of Hahn and Meitner, showed that of the three naturally occurring isotopes of uranium (viz., those of mass numbers 234, 235 and 238) the only one which undergoes fission under neutron bombardment is that of mass number 235 (now usually referred to as U-235, or uranium-235). This isotope occurs in natural uranium to the extent of 0.719 per cent only.

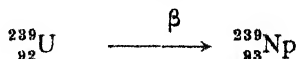
A striking and important feature of the fission process, in addition to the enormous quantity of energy evolved, is the fact that the process itself produces neutrons and, on the average, the number of neutrons emitted in each fission (initiated by one neutron) is greater than one. Hence, the process can start a chain reaction which can produce enormous amounts of energy in a very small fraction of time. This is the principle of the "atomic bomb," for the first of which (that released at Hiroshima on 6th August 1945) the isolation of uranium-235 in a state of purity was necessary. It is also the principle behind the various forms of *nuclear reactor* for the utilization of atomic energy for peaceful purposes which are discussed further below (page 173).

The isolation of uranium-235 was a tremendous undertaking, enormously expensive both in time and money, but it was successfully achieved by the use of the fractional diffusion of gaseous uranium hexafluoride at a temperature of 140° C. Many thousands of stages were necessary in the diffusion process; some idea of the immensity of the problem may be gained from the facts that the plant at Oak Ridge, California, where this work was done, is four storeys high and covers an area of 60 acres.

Two other nuclei are known which undergo fission under neutron bombardment but neither occurs naturally. These are plutonium,  $^{239}_{94}\text{Pu}$ , and uranium-233,  $^{233}_{92}\text{U}$ . The former is produced as a result of the bombardment of the abundant isotope of uranium,  $^{238}_{92}\text{U}$ . Uranium-238 can undergo fission under the bombardment of fast neutrons but the slow neutrons are captured and produce a new nucleus as indicated by the equation



The uranium-239 thus formed is radioactive and decays, with a half-life period of 23.5 minutes, with the emission of an electron

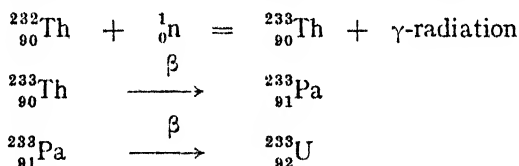


the product being the trans-uranium element called neptunium. This in turn decays, with a half-life period of 2.3 days, forming plutonium in a further  $\beta$ -ray change



Plutonium is itself radioactive, but its half-life period is  $2.4 \times 10^4$  years. Plutonium, being a new element with different chemical properties, can be separated from the natural uranium from which it is formed by chemical methods and it is thus much more easily isolated than uranium-235. The apparatus necessary for its production is that of the *breeder reactor* and is described below (page 173). Plutonium, obtained in this way, was the material used in the second "atomic bomb," that released over Nagasaki on 9th August 1945.

Uranium-233 results from a similar sequence of changes, beginning with natural thorium. These are represented as follows:



The half-life period of thorium-233 is 23.5 minutes; that of protoactinium-233, 27.4 days and of uranium-233,  $1.6 \times 10^5$  years. So far, uranium-233 has not been used to any extent in atomic energy projects but it is likely to become of importance in the future since the thorium from which it is produced is believed to occur naturally in greater abundance than uranium and, in any case, it will thus provide an additional source of nuclear "fuel."

### § 5 Applications of Nuclear Fission. The Release of Atomic Energy

When nuclei of uranium-235 undergo fission two new nuclei are produced. It has been found that different atoms split in different ways so that a variety of products results from the action of neutrons on a quantity of a fissionable element. So far about forty different elements have been identified among the products of the fission of uranium-235 ranging from molybdenum to the rare earths.

The energy liberated when one gram of uranium-235 undergoes fission has been calculated to be equivalent to that released by the combustion of 18 tons of coal. This energy, which corresponds to a loss of mass in the process of about 0.1 per cent of the uranium-235 which has been

split, appears partly (about 88 per cent) in the form of kinetic energy and partly (approximately 12 per cent) as  $\gamma$ -radiation. This  $\gamma$ -radiation is of very high energy, it is very penetrating and extremely destructive.

As mentioned already neutrons are emitted in the course of fission and they are produced, not only in greater numbers than those necessary to initiate the process, but also with high energy. In some of the fissions which have been detected it can be shown that three neutrons would be expected to be released from each uranium-235 nucleus which breaks up. Actual experiments have shown that the *average* number of neutrons produced is 2.5. The way in which, under suitable conditions, a chain reaction can be built up by neutrons released in this way is illustrated by Fig. 12.2.

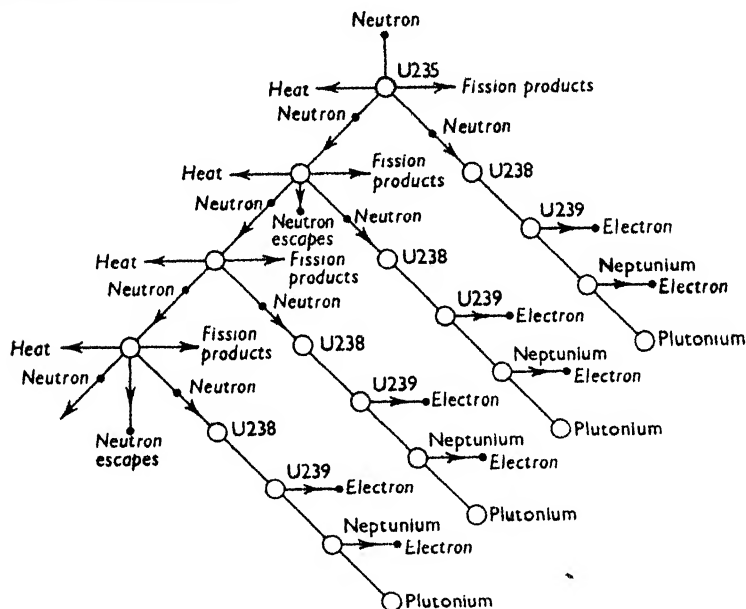


FIG 12 2 —Chain Reactions built up by Neutrons  
(Redrawn from Jay, Calder Hall, by permission of the Atomic Energy Commission)

The very small proportion of fissionable nuclei in natural uranium (0.719 per cent) is one reason why a chain reaction of fissions does not develop spontaneously in pure uranium. In addition, the uranium-238 present, which is present in preponderating amount, absorbs neutrons strongly especially the high-speed neutrons which are produced by the fission of uranium-235. One method for producing and sustaining a chain reaction is, as has been seen, to isolate the uranium-235 from the natural material, as was done for the first atomic bomb. Even with

pure uranium-235 there is a critical size for a spherical piece of the material below which the chain reaction will not be sustained on account of the escape of neutrons from the lump without causing fission. This critical size, which is a very closely guarded secret, is quite small. This is the principle of the **fast reactor** of which the extreme and completely uncontrolled form is the atomic bomb.

Uranium-238 easily absorbs the fast neutrons (travelling at about  $15 \times 10^6$  cm. per second) released in the casual fissions of uranium-235 nuclei in the natural material. But slow neutrons, which are more effective in causing fission of uranium-235 than the fast neutrons and, if slow enough, will produce fission more rapidly than the resultant neutrons, are absorbed by the uranium-238. This property is made use of in the **slow reactor** (of which BEPO, the first experimental reactor to be built at the Atomic Energy Research Establishment at Harwell, is a famous example).

Fermi showed in 1935 that neutrons can be slowed down by collision with other light particles such as atoms of hydrogen, beryllium and carbon. A material used for the purpose of slowing down neutrons is

known as a **moderator**. Fermi constructed the first slow reactor by using graphite bricks as moderator, in 1942, and by careful adjustment of the sizes and dispositions of the graphite and uranium was successful in producing a chain reaction in natural uranium. BEPO, the Harwell reactor mentioned above, similarly uses graphite bricks as moderator and this has given rise to the alternative name, **pile**, for such a reactor.

The diagram (Fig. 12.3) shows the principles on which this reactor is constructed.

It consists of a cube of graphite (constructed from graphite bricks) of 26-foot side. This cube is penetrated by a series of cylindrical holes, in some of which at the centre of the cube aluminium cylinders containing uranium are placed. Other similar channels are

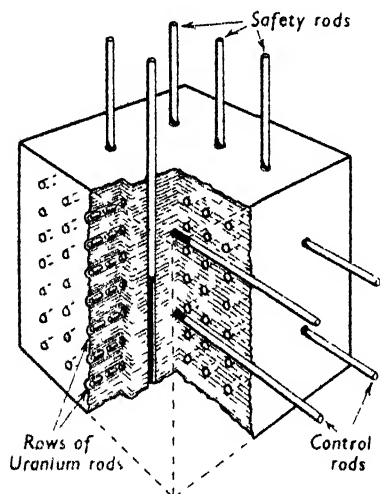


FIG 12.3.—British Experimental Pile (BEPO)

(Redrawn from Jay, Calder Hall, by permission of the Atomic Energy Commission)

available for the insertion of materials to be irradiated by the intense neutron flux existing when the pile is operating and to provide beams of neutrons for experimental purposes. To bring this pile to a critical state when the chain reaction begins requires 28 tons of uranium;



the charge can be raised to 40 tons when the output of energy will be equivalent to about 6000 kilowatts. The rate at which the reactor operates is controlled by means of a system of hollow steel rods, filled with boron carbide which absorbs neutrons very strongly. These rods are pushed in and out of suitable channels in the graphite cube and the reactor can be maintained very accurately at a predetermined level of activity by automatic control of the positions of these rods. The pile is cooled by the circulation through it of a very large volume of air, and for protection of the surroundings from radiation it is enclosed completely in thick layers of concrete and steel.

The same principle, viz., the graphite-moderated slow reactor, has been adopted at the Calder Hall "Atomic" Power Station; the first in the world to supply commercial electrical energy based on nuclear energy as its prime source. At Calder Hall, however, the transference of heat from the reactors to the boilers for raising steam for the generation of electricity is effected, not by means of air, but by means of carbon dioxide at a pressure of about 100 lb. per square inch.

Among applications in medicine some interesting types are the use of radioactive iodine in the treatment of goitre, and of a phosphorous isotope in the treatment of certain diseases of the blood-stream. In addition radioactive cobalt-60 is taking the place of radium (or radium emanation) in the treatment of cancer.

All these developments are of comparatively recent date and there can be no doubt that there will be great extensions in the use of artificial isotopes in the future.

### § 6 Fast Breeder and Other Reactors

It has been mentioned above that in certain circumstances plutonium, an artificially produced radioactive element, is able to undergo fission when bombarded with neutrons. It is possible to use the neutrons resulting from the fission of uranium-235 to produce plutonium from uranium-238 (the main constituent of natural uranium) and at the same time to liberate energy. A reactor designed for this purpose is known as a **breeder reactor** and may be used as a source of power while producing further quantities of fissionable material. An obvious advantage of such a reactor, in comparison with the so-called "slow reactor" already described, is the much greater ultimate utilization of the natural "fuel" (viz., uranium) which it makes possible.

A fast\* breeder reactor cannot be operated with uranium containing only the naturally occurring proportion of fissionable material; an enriched fuel is necessary and the enrichment may be with uranium-235 extracted from the naturally occurring ore (the necessary beginning, obviously) or, once the whole process is under way, by means of plutonium and, perhaps, in the future, with uranium-233 obtained similarly from thorium.

\* i.e., using high-speed neutrons.

The technical and engineering problems involved in building a full-size fast breeder reactor designed to produce power also are very great and so an experimental reactor is being built at Dounreay on the north coast of Scotland in order that the possibilities of such a project may be fully studied. To begin with natural uranium enriched with uranium-235 will be used as the nuclear "fuel" and will be contained in a core 21 inches in diameter and 21 inches high consisting of enriched uranium rods sheathed in niobium containers. Surrounding this will be a breeder blanket composed of 2000 rods of natural uranium each eight feet long and one and a quarter inches in diameter contained in stainless steel cans. The heat developed is to be transferred by means of a liquid sodium-potassium alloy and control will be effected by moving groups of "fuel" elements into, or out of, the core. The plant is designed to produce an output of 60,000 kilowatts of electrical energy and, in time, substantial quantities of plutonium as well.

The Calder Hall type of reactor, using natural uranium, produces the heat equivalent of 10,000 tons of coal from one ton of uranium; it is calculated that it should be possible, in due course, to design a fast breeder reactor which will develop power equal to that of one million tons of coal from one ton of uranium.

A great variety of types of reactor is theoretically possible, and the theoretical and practical problems involved in the design and construction of some of them are being actively investigated at Harwell, Risley and elsewhere. Among these may be mentioned reactors using slow neutrons in which the moderator is heavy water or beryllium; different arrangements of the fissile material are possible, either heterogeneous, with rods, for example, or homogeneous, where the chain reaction takes place in a liquid solution. Considerable variety is also possible in the cooling medium used for the transfer of heat; in addition to the use of air, or other gas, and liquid sodium-potassium alloy already mentioned, oil and heavy water have also been suggested. Altogether, it is thought that there are about one hundred different kinds of reactor which might be made and experimental reactors of small scale are already in being or under construction to investigate some of these numerous possibilities.

### § 7 Uses of Artificial Isotopes

The fission process, as operated in a nuclear reactor, or pile, produces a large number of radioactive isotopes of elements in the middle range of the Periodic Table. Thus, in one investigation it was found that the breakdown of 100 atoms of uranium-235 produced 87 isotopes of 34 elements. In addition many other isotopes can be obtained by exposing other elements to the intense neutron flux which exists in the centre of a reactor in operation. It is noted (on page 172) that the construction of BEPO includes channels in the core for this very purpose.

The availability of these isotopes has resulted in many valuable

applications in scientific research, in industry and in medicine. In the course of chemical research they are valuable as a means by which particular atoms may be "labelled" and thus provide a means for following the course, or mechanism, of reactions which cannot be elucidated in any other way. A recent development of great interest is the investigation of the carbon-14 content of organic materials such as wood, as a means of dating objects of archaeological importance.

In industry, isotopes have found numerous and varied applications, among which may be mentioned the investigation of the wearing of motor tyres and of various parts of machinery in general, the following of the course of fluids in pipelines (e.g., for the long-distance transport of oil where a change in the type of oil being pumped is indicated by the presence of a trace of a different radioactive isotope), the structure of oil-wells, the silting of rivers and following the course of the polymerization reactions which are the basis of the plastics industry. In addition the use of polonium-210 is superseding that of radium in the manufacture of luminous enamels (cf. page 713).

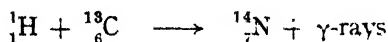
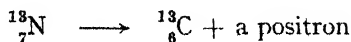
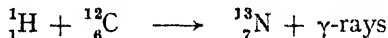
### § 8 Nuclear Fusion

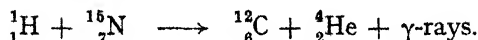
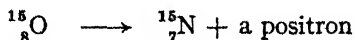
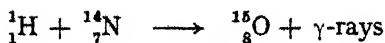
The energy liberated as a result of nuclear fission arises from the loss of mass which occurs when a heavy atom, such as uranium, breaks up. A similar loss of mass, accompanied again by the release of large amounts of energy, occurs when helium is formed from hydrogen and in similar nuclear reactions. This process is referred to as nuclear fusion and is believed to be the source of the enormous amounts of energy radiated by the sun and the stars. These reactions can only occur in a region of very high temperature in order that the atoms shall have sufficient velocity to undergo nuclear reactions; at a temperature of a few million degrees, such as obtains in the sun, the atoms are moving with an energy sufficient to bring about nuclear reactions.

The over-all process

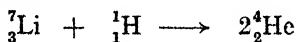


is believed to be the principal one but it cannot occur so directly and simply since the hydrogen nucleus contains no neutrons and the helium nucleus contains two. It is supposed, therefore, that a series of nuclear reactions occurs involving carbon which, being re-formed, acts as a kind of catalyst for the synthesis of helium from hydrogen, thus:





The production of the hydrogen bomb, or thermo-nuclear bomb, involves bringing about the formation of helium from hydrogen very suddenly. The above cycle, it is believed, would be too slow for this purpose and some such reaction as



is probably used. The necessary extremely high temperature for the initiation of this reaction is probably attained by means of a small-scale atomic fission type of bomb in the mixture from which the helium is to be made.

If the nuclear fusion reaction can be tamed, in the sense that the atomic bomb of the fission type has been tamed in the power reactor, the world's hydrogen (almost inexhaustible in its water supplies) will be available to serve its requirements of energy when its uranium is getting low. Sir John Cockcroft has suggested that this problem, also, might be solved within the next 2000 years; more recently still much more optimistic estimates of the time required have been made.

## CHAPTER 13

# SOLUTION AND CRYSTALLIZATION

In the strictly scientific sense of the word insolubility does not exist, and even those substances characterized by the most obstinate resistance to the solvent action of water may properly be designated as extraordinarily difficult of solution, not as insoluble.—O. N. WITT.

### § 1 General Classification

THE behaviour of solids such as sugar or salt when brought into contact with water is a familiar fact of experience. The solid seems to disappear into the liquid, and we say that it has **dissolved**, while the resulting homogeneous mixture is termed a **solution**. The dissolved substance is often called the **solute** and the liquid in which it is dissolved, the **solvent**.

Solutions are thus a particular kind of mixture, but are not confined to mixtures of solids and liquids. Thus we can have:

Solutions of solids	in	solids	
"	"	"	" liquids
"	"	"	" gases
"	"	liquids	" solids
"	"	"	" liquids
"	"	"	" gases
"	"	gases	" solids
"	"	"	" liquids
"	"	"	" gases

The solution of a solid in a liquid is the most familiar type and hence serves best as a starting point for the study of solutions.

### § 2 Solutions of Solids in Liquids

A mixture of a solid and a liquid may be one of three types, which shade off into each other almost imperceptibly. These types are: true solutions, colloidal solutions and suspensions.

If a small quantity of a salt, such as potassium iodide, be added to a fixed quantity of water and the mixture stirred, the solid seems to disappear. Further small quantities of potassium iodide can be added with the same result. A similar experiment with a coloured salt such as potassium dichromate shows that the lump of coloured solid gradually disappears but the liquid becomes coloured. In all such cases there is found to be a limit beyond which (at a given temperature) no more solid will pass into the liquid. Within this limit the mixtures

formed appear homogeneous to the ordinary sight and are called **simple, true solutions**. They are believed to contain either single molecules or parts of molecules. (Cf. Chapter 15, page 218.)

In such a solution the solid does not separate under gravity, and is not removed by ordinary filtration, but can be recovered on evaporation.

**Suspensions** consist of gross particles of a solid surrounded by the liquid. These gross particles settle out under gravity, are easily visible (often to the naked eye; always under the microscope), and can be easily removed by ordinary filtration.

There exists also a class of solid-liquid mixtures in which the particles of solid are intermediate in size between the single molecules (or parts of molecules) of true solutions, and the gross particles present in suspensions. These are known as **colloidal solutions**. In them the particles of solid, which carry an electric charge, do not settle under gravity and are not easily removed by ordinary filtration. They consist of aggregates of relatively small numbers of molecules. The properties of these colloidal solutions are dealt with more fully in Chapter 19.

In the absence of chemical combination, gases are miscible in all proportions and the properties of a gas mixture (or solution) are those of its constituents. (Cf. Chapter 3.) But, as mentioned already, there is, in general, a limit to the amount of a given solid which will dissolve in a fixed amount of a particular liquid at any particular temperature. For example, if potassium chloride be added to water kept at a constant temperature, the salt is gradually dissolved, and the process of solution continues until a definite amount has dissolved. The amount of solid remaining in excess of this will remain an indefinite time without further change, provided the temperature remains constant, and no solvent is lost by evaporation. The solid and solution are then in equilibrium. As in the analogous case of the vapour pressure of a liquid (see page 140), the equilibrium between a saturated solution and a solid is dynamic, not static. The solution is said to be **saturated** with the salt at the temperature of experiment. **The weight of salt dissolved by 100 gm. of the solvent so as to make a saturated solution at any assigned temperature is called the solubility of the salt.\*** Thus, 100 gm. of water at 20° will dissolve 35 gm. of potassium chloride, and accordingly, 35 is the solubility of potassium chloride in water at 20°.

### § 3 Determination of the Solubility of a Solid in a Liquid

The weight of a given solid which will dissolve in a fixed weight of any particular solvent is limited; and further experiments such as those about to be described show that this limit is a constant for a given pair of substances, so long as the temperature remains

\* Other modes of representing solubility are more convenient in special cases—e.g., in Fig. 13.3 the percentage amount of salt in a given weight of the solution is employed.

constant. The determination of solubilities is, therefore, a matter of importance.

The usual method consists in the preparation of a saturated solution of the substance at the desired temperature, and the analysis of a known amount of the solution so obtained. This is carried out in an apparatus such as that shown diagrammatically in Fig. 13.1.

An excess of the finely-powdered solid is placed in a bottle, through the stopper of which there passes a thermometer, a mechanical stirrer and a stoppered tube by means of which a pipette may be inserted. Pure solvent (e.g., distilled water) is added, and the whole is immersed in a thermostat (i.e., a large bath of water automatically maintained at a previously determined temperature) whose temperature has been adjusted to that at which the solubility is to be determined. The mixture of solid and solvent is then vigorously stirred for some hours, or even days. At the end of a suitably long period the stirrer is stopped and, after several hours during which time all undissolved solid has settled, a pipette, warmed to slightly above thermostat temperature and fitted with a filter, is inserted and a portion of the saturated solution is withdrawn by means of it. This solution is then transferred to a weighed vessel, and the weight of the solution determined, after which it may either be analysed chemically, or very carefully evaporated to dryness if the compound concerned is such that it undergoes no change during evaporation. The weight of solid which has been dissolved in a known weight of solution can then be determined, and hence the weight of solid dissolved in 100 gm. of water may be found.

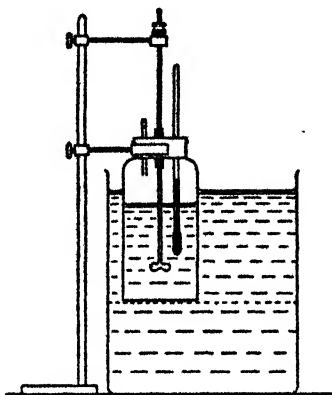


FIG. 13.1.—Determination of the Solubility of a Solid

The calculations involved can be understood from the following example:

*In an experiment for the determination of the solubility of oxalic acid 16.37 gm. of solution saturated at 20° C. were diluted to 500 ml. 25 ml. of this solution were titrated with a decinormal solution of barium hydroxide and were found to require 15.8 ml. for neutralization. Calculate the solubility of oxalic acid at 20° C.*

15.8 ml. of decinormal barium hydroxide solution contain 0.00158 equivalents of barium hydroxide.

∴ 25 ml. of the dilute oxalic acid solution contain 0.00158 equivalents of oxalic acid.

But the equivalent of oxalic acid is 45.  $\therefore$  500 ml. of diluted oxalic acid solution contain  $\frac{0.00158 \times 500}{25}$  equivalents of oxalic acid

$$= \frac{0.00158 \times 500 \times 45}{25} \text{ gm. of oxalic acid}$$

$$= 1.422 \text{ gm. of oxalic acid.}$$

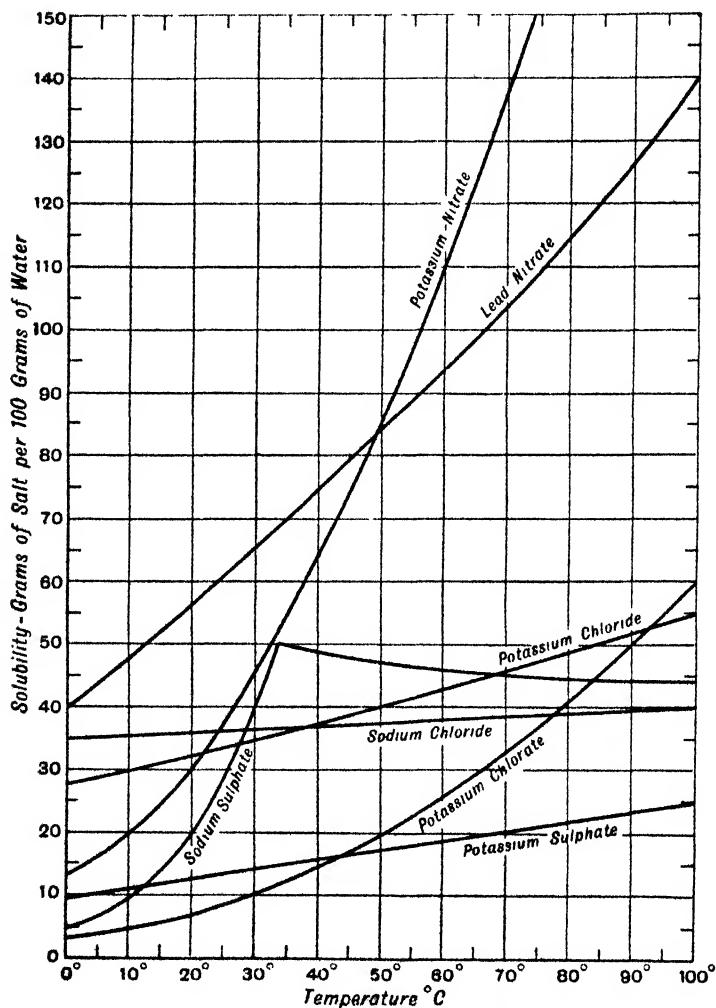


FIG. 13.2.—Solubility Curves



∴ 16.37 gm. of saturated solution contain 1.422 gm. of oxalic acid,

∴ 16.37 – 1.422 gm. of water dissolve 1.422 gm. of oxalic acid,

i.e., 100 gm. of water dissolve  $\frac{1.422 \times 100}{14.948}$  gm. of oxalic acid.

∴ The solubility of oxalic acid at 20° C. is 9.51 gm. per 100 gm. of water.

The solubility of a substance determined as above is found to vary, in general, with temperature, a rise in temperature usually causing an increase in solubility. When the solubility of a solid has been found for various temperatures, the relation between solubility and temperature can be plotted in the form of a graph. Such a graph is known as a solubility curve, and some typical solubility curves are shown in Fig. 13.2.

Curves such as these show that:

- (i) solubility usually increases with increase of temperature;
- (ii) the effect of change of temperature on the solubility is different for different substances;
- (iii) the change is usually gradual, but sometimes (e.g., sodium sulphate, Fig. 13.3) the curves show sudden changes in direction (see below, page 182).

#### § 4 Purification by Crystallization

The considerable difference in the solubility of a given solid at different temperatures provides a convenient means for the purification of soluble substances.

If the impurity consists of a small quantity of an insoluble substance, the process consists in making a solution which is saturated or nearly saturated when hot, filtering it rapidly, and allowing the filtrate to cool, when the dissolved substance will crystallize out on cooling. This process is known as **recrystallization** and is of great importance in chemistry.

If the impurity which it is desired to remove is a soluble one, the process of recrystallization can often still be employed, particularly if one substance is present in only small proportion, or if the solubility curves of the two substances are sufficiently divergent.

In the former case the constituent present in small quantity will not, in general, be present in amount sufficient to saturate the solvent employed even at room temperature, and hence it remains in solution on cooling.

The principle involved in the latter case may be explained by an actual example. Suppose that it is desired to separate a mixture of equal quantities (say 30 gm.) of potassium chloride and potassium chlorate. Reference to Fig. 13.2 on page 180 shows that at room temperature the solubilities of these are about 30 and 5 respectively, while at a temperature between 70° and 80° C. the solubilities are about

35 and 50 respectively. If, therefore, we dissolve our mixture in 100 c.c. of water at about  $75^{\circ}\text{C}$ . and allow the solution to cool, we shall find that potassium chlorate will separate at once, while potassium chloride (and a little potassium chlorate) will remain in solution, since the quantity of potassium chloride present barely reaches the amount required for a saturated solution even at room temperature. The chlorate will actually contain entangled traces of chloride which can be removed by a further recrystallization as described in the previous paragraph.

The solution from which the potassium chlorate has been removed will now contain approximately 30 grams of potassium chloride and 5 grams of potassium chlorate. If this solution be evaporated until it begins to crystallize, and then allowed to cool, potassium chloride will be deposited, contaminated with a trace of potassium chlorate. Again recrystallization will enable a pure specimen of potassium chloride to be obtained.

### § 5 Abnormal Solubility Curves

Usually solubility curves are smooth: there are no sudden breaks in them. Sometimes, however, the curve showing the relation between solubility and temperature does exhibit sharp and sudden breaks or changes in direction.

An example of such a curve is that for sodium sulphate shown in Fig. 13.3.

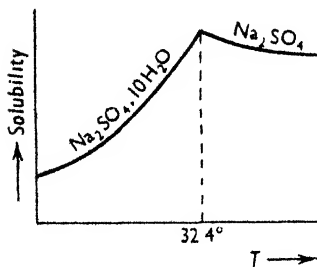
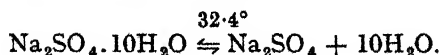


FIG 13.3.  
Solubility Curve of Sodium Sulphate

On examining this graph we see that the solubility *increases* rapidly at first with rise of temperature, as shown by the slope of the curve, Fig. 13.3. There is an abrupt change in the direction of the solubility curve at  $32.4^{\circ}\text{C}$ . Above that temperature the solubility *decreases* with rise of temperature. The interpretation is that the solubility curve is really compounded of two solubility curves. Sodium sulphate is a *hydrated salt*, that is, it crystallizes with *water of crystallization* (page 319); as ordinarily obtained, ten molecules of water are present along with one molecule of sodium sulphate. Thus

in the diagram the curve of increasing solubility with rise of temperature below  $32.4^{\circ}$  represents the solubility curve of the decahydrate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; and the curve of decreasing solubility with rise of temperature represents the solubility curve of the anhydrous salt,  $\text{Na}_2\text{SO}_4$ , in rhombic crystals. The decahydrate, at  $32.4^{\circ}$ , is transformed into the anhydrous salt. The decahydrate is not stable above  $32.4^{\circ}$ ; the anhydrous salt is not stable below  $32.4^{\circ}$ . This temperature is

called the **transition temperature** or **transition point**, and the change is symbolized



The solubility curves, it will be observed, represent the condition of equilibrium between the solvent and salt.

It makes no difference whether we start with the anhydrous sulphate or the decahydrate. When in equilibrium, the solution in contact with the solid will contain the amounts of sodium sulphate— $\text{Na}_2\text{SO}_4$ —indicated by the solubility curves. The saturated solutions, when in equilibrium, have the same concentration and are identical in every way. We cannot continue the observation of the solubility of the decahydrate beyond  $32.4^\circ$  because it *immediately* splits up into the anhydrous form; but since the transformation of the anhydrous salt into the hydrate takes an appreciable time, it is possible to measure the solubility of the anhydrous salt below  $32.4^\circ$ .

The solubilities of the two sodium sulphates—anhydrous and decahydrate—are quite different. At  $32.4^\circ$  the rhombic sodium sulphate passes into the monoclinic form with its own solubility curve. If the solid decahydrate were in contact with a saturated solution at  $20^\circ$ , and some of the anhydrous sulphate were added to the solution, some of the anhydrous sulphate would dissolve and be deposited later as the decahydrate. The final result would be a transformation, through the medium of the solution, of the anhydrous salt into the decahydrate.

Apparently abnormal solubility curves result also from the formation of double salts.

It is often found that if two simple salts are mixed in water and the mixed solution is then allowed to crystallize, a salt is obtained which is a compound of both salts. For example, such a mixture of potassium sulphate and aluminium sulphate in solution will, when allowed to crystallize, deposit a compound of the formula  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$  known as alum. Such a compound is called a **double salt** if, in solution, it gives the reactions of all the radicals present. (Compare complex salts, page 946.)

## § 6 The Freezing of Solutions

It has long been known, even as far back as Aristotle's day, that drinkable water could be obtained from frozen sea-water; and that, if an aqueous solution of salt be gradually cooled, comparatively pure ice first separates from the solution. The trace of salt generally found in ice which has separated from sea-water is mechanically entangled in the ice.

The curve *OB*, Fig. 13.4, represents the solubility of potassium chloride at temperatures ranging from  $-10.64^\circ$  to  $+60^\circ$ ; the

observation cannot be continued below  $-10.64^{\circ}$  because at that temperature the whole mass freezes; the upward curve would probably stop only at the melting point of potassium chloride if it were not for the volatilization of the water.

The freezing temperature of a solution is generally lower than that of the pure solvent. As long ago as 1788, C. Blagden cited a number of observations which led him to the belief that the lowering of the

freezing point is proportional to the amount of substance in solution. In Blagden's own words: **The effect of a salt is to depress the freezing point in the simple ratio of the proportion to water.** This generalization is sometimes called **Blagden's Law**. The freezing point of an aqueous solution of potassium chloride, that is, the temperature at which ice begins to separate, is gradually reduced by the continued addition of small quantities of potassium chloride, and reaches its lowest value,  $-10.64^{\circ}$ , when the solution has nearly 19.5 per cent of

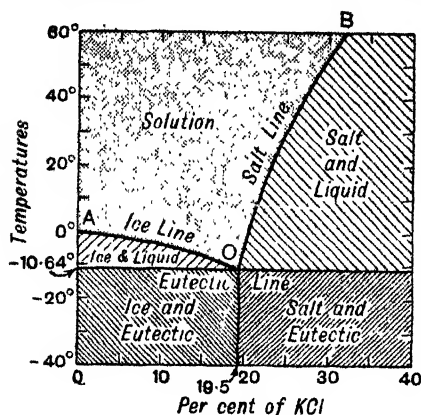


FIG. 13.4.—Solubility and Freezing Curve of Potassium Chloride and Water Solutions.

potassium chloride; further additions of the salt raise the temperature at which solid separates. *Solid potassium chloride*, not ice, then separates from the solution.

Imagine a 5 per cent solution of potassium chloride subjected to a gradually diminishing temperature. Start at  $0^{\circ}$ . When the temperature reaches, say,  $-4^{\circ}$ , ice separates from the solution. The mother liquid remaining has therefore more than 5 per cent of salt in solution; as the temperature falls, more ice separates. The further concentration of the mother liquid and the separation of ice continue until the mother liquid has about 19.5 per cent of potassium chloride, when the whole remaining liquid freezes *en bloc* at  $-10.64^{\circ}$ . Quite an analogous series of changes occurs if solutions containing more than 19.5 per cent of potassium chloride be gradually cooled. This time, however, instead of pure ice, pure potassium chloride separates until the residual liquid has 19.5 per cent of potassium chloride, when the whole solidifies *en masse* at  $-10.64^{\circ}$ . If the cooling solution has just 19.5 per cent of salt, neither ice nor salt separates until the temperature has fallen to  $-10.64^{\circ}$ , when the whole freezes to a solid mass. No other mixture of water and potassium chloride freezes at a lower temperature than this. This solution containing 19.5 per cent of potassium chloride is called a **eutectic mixture**; and  $-10.64^{\circ}$  the

**eutectic temperature.** F. Guthrie used to think that this mixture—water with 19.5 per cent of potassium chloride—corresponded with the formation of a definite compound of potassium chloride and water, stable only at low temperatures. Hence his designation **cryohydrate** for the alleged compound. The term “eutectic mixture” is now preferred in place of cryohydrate, for we now know that these cryohydrates are not compounds but only mechanical mixtures of ice and salt. The evidence for this conclusion may be summarized as follows: (1) The heterogeneous structure is frequently apparent under the microscope. (2) Unlike true crystalline compounds, the cryohydrates are generally opaque and ill-defined. (3) Alcohol may dissolve the solvent, leaving behind a network of salt. (4) There are no special signs of chemical change during the formation of the cryohydrate. (5) The ratio of salt to solvent is not always in molecular proportions. The agreement in some cases is merely a coincidence. (6) The composition of a cryohydrate is different when the solidification takes place under different pressures.

### § 7 Gibbs's Phase Rule

J. Willard Gibbs (1876–8) discovered an important generalization which is known as the **Phase Rule**, and it has wide applications in the study of solubility and many other phenomena.

The Phase Rule deals with the behaviour of heterogeneous systems at equilibrium, and it employs three special terms, viz., phase, component, and degree of freedom or variance.

A heterogeneous system is made up of different portions; each of these is homogeneous in itself but is separated from the others by surfaces. Each of these portions is called a **phase**. Thus in the case of aqueous solutions of potassium chloride, the eutectic contained two phases—KCl and  $H_2O$ . With an aqueous solution of sodium sulphate at the transition point, Fig. 13.3, we had to deal with four phases— $Na_2SO_4$ ,  $Na_2SO_4 \cdot 10H_2O$ ; the saturated solution; and the vapour arising from the solution. With freezing water, we have the three phases: ice, water, and vapour. In homogeneous systems there can only be one phase, e.g., gaseous systems; and in heterogeneous systems there are always two or more phases.

The conception of a **component** is rather more difficult to explain. The components of a system are taken to be the least number of independently variable constituents by means of which the composition of each phase in the form of a chemical equation can be expressed.

The components may be elements or compounds which behave in a system, for the time being, *as if* they were elements. There is only one component in the system just considered, namely, water— $H_2O$ ; the components in the system considered in the previous section—an aqueous solution of potassium chloride—are water ( $H_2O$ ) and potassium chloride (KCl); and two components were involved in our study of the solubility of sodium sulphate, namely, water ( $H_2O$ ) and sodium sulphate ( $Na_2SO_4$ ). (See also page 245 for a further example.)

The **degree of freedom** of a system—sometimes called the **variance** of a system—is the number of independent variables which must be fixed before the state of the system can be defined without ambiguity.

**Variance or degrees of freedom of a system.**—It will be remembered that the condition of equilibrium of a gas with respect to temperature, pressure, and volume was defined (on page 26) by the equation  $pV = RT$ , where  $R$  is a numerical constant whose value depends upon the units of measurement (page 26). If

only one of these variables be fixed, say the volume, the state of the system will remain undefined, because the gas can retain one fixed volume, and yet have very different values for temperature and pressure. Two of the three variables must be known before the state of the system can be defined unequivocally, without ambiguity. If any two of the three variables be fixed, the third variable can only assume one definite value. The two fixed variables are said to be arbitrary or **independent variables**; the third variable which can be calculated from the condition of equilibrium ( $pv = RT$ ) when the two independent variables are known, is called the **dependent variable**. The gaseous system under consideration has two degrees of freedom.

With these terms clear in our minds we can now state the **Phase Rule** which is that a system will be in equilibrium when its variance is equal to the number of components in the system less the number of phases, increased by two. In symbols:  $F = C - P + 2$  where  $C$  denotes the number of components,  $P$  the number of phases, and  $F$  the variance or degrees of freedom of the system.

Its application may be illustrated by consideration of the behaviour of water.

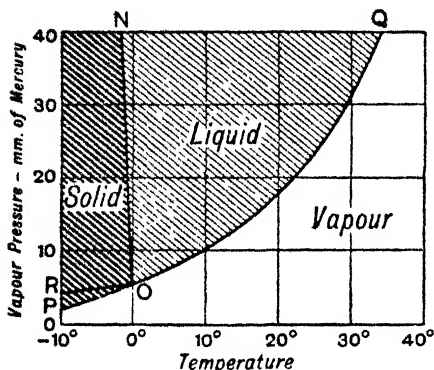


FIG. 13.5—Vapour Pressure Curves of Water

Fig. 13.5 shows the relation between the vapour pressure of water and the temperature.

The system consisting of liquid water and vapour has two variables: vapour pressure and temperature. So long as liquid water is present, the pressure is determined solely by its temperature; given either the pressure or the temperature, the other can be determined from the relation symbolized in the vapour pressure curve—Fig. 13.5. Hence the state of the system is defined by two variables—the one is dependent, the other independent. In other words, the system has one degree of freedom, that is, the system is **univariant** for  $C = 1$  and  $P = 2$  as there is only one component "water" in two phases, liquid and vapour.

The three curves  $PO$ ,  $OQ$ , and  $ON$ —Fig. 13.5—represent the conditions of equilibrium of three two-phase systems. solid-vapour, vapour-liquid, and solid-liquid respectively. These three curves meet at the point  $O$ . Here three phases can coexist in equilibrium. Hence the point  $O$  is called a **triple point**. The co-ordinates of the triple point are: pressure, 4.57 mm.; temperature, 0.0076° C. If the pressure or temperature be altered ever so little, one of the phases—ice or liquid water—will disappear and a two-phase univariant system represented by a point on one of the curves  $OP$ ,  $OQ$ ,  $ON$  will appear. At the triple point the system is **invariant**, for here  $C = 1$  as before, and  $P = 3$ , as there are now three phases: solid, liquid, and vapour.

If a system is such that it has two degrees of freedom—i.e., it is **bivariant**—it follows from the Phase Rule that  $P = C$ . Two variables must be known before the state of the system can be determined. A saturated solution in the presence of an excess of the solute is univariant, but bivariant if not saturated. In the former case there are two components and three phases—solid, solution, and vapour; in the latter case there are two components and two phases. Hence in the one case,  $F = 2 + 2 - 3$ ; and in the other,  $F = 2 + 2 - 2$ . Again, in the region  $PON$ , Fig. 13.5, the system will be bivariant, because there is only one phase and one component. Pressure and temperature may be altered without interfering with the state of the aggregation of the ice so long as the variations keep within the boundary lines  $PO$  and  $ON$ . The same remarks may be

applied to the condition of the water represented by points in the regions *NOQ* and *POQ*.

The Phase Rule is therefore a method of grouping systems which behave in a similar manner into one class. It is essentially a system for the classification of states of equilibrium. Systems having the same variance behave in an analogous manner under the influence of variations in temperature, pressure, and volume or concentration. It makes no difference whether the changes be chemical or physical. As indicated above, the Phase Rule also tells us whether the phases of a heterogeneous system are those necessary for equilibrium.

### § 8 Solutions of Solids in Solids

If an aqueous solution containing both potash alum (page 751) and chrome alum (page 875) be allowed to crystallize, only one type of crystal is deposited and these crystals are found to contain ions of both chromium and aluminium as well as potassium ions and sulphate ions. The constitution of these crystals is represented as  $R_2SO_4 \cdot (Cr, Al)_2(SO_4)_3 \cdot 24H_2O$ , since the proportions in which the chromium and aluminium are present depend upon their relative amounts in the original solution. Another example is furnished by the crystallization of mixed solutions of potassium perchlorate and potassium permanganate. Properties of these crystals, such as density and colour, vary according to the proportion of each compound present. Such crystals are said to be **solid solutions**; they are sometimes known as *mixed crystals*, but this is an unsatisfactory term as it might be thought to imply the presence of different kinds of crystal mixed together, whereas, in fact, solid solutions consist of one sort of crystal only. Other important examples of solid solution are the metal alloys, e.g., brass.

### § 9 Solutions of Liquids in Liquids

In many ways mixtures of liquids exhibit a behaviour similar to that of mixtures of solids and liquids such as we have been discussing in the preceding sections. Thus some, such as mercury and water, are practically **immiscible**; others, such as water and sulphuric acid, are **completely miscible**. With some pairs of liquids, again, as for instance water and ether, each liquid dissolves to a limited extent in the other: they are **partially miscible**.

The immiscibility of mercury and water is analogous to the insolubility of a solid (like sand) in water; the partial miscibility of ether and water is analogous to the mixing of excess of salt with water—a solution of salt is formed and at the same time the solid salt is wet. Thus, if successive small quantities of ether are added to water, they dissolve completely at first; but after a time a point is reached when, the water being saturated with ether, the addition of a further quantity causes the separation of a layer of ether which floats on the top of the aqueous solution. But this upper layer is not merely pure ether (in the sense that a solid in contact with its saturated solution is a pure substance) for the ether layer dissolves some water, as indeed can be easily seen by the addition of a little water to dry ether—the water dissolves completely. Thus, the two layers are respectively a saturated solution of ether in water, and a saturated solution of water in ether, and, provided the temperature is not

altered, the percentage composition of both will remain constant even if more ether be added. This addition will cause, however, a change in the relative bulk of the layers, the ether layer (solution of water in ether) will gradually grow, and the water layer will gradually diminish until it finally disappears, when we have left a homogeneous solution of water in ether. It is to be noted, also, that increase of temperature usually increases the miscibility; this is analogous to the increase in solubility of solids in liquids with rise of temperature.

### § 10 Separation of Mixed Liquids

The separation of mixed liquids or the recovery of a solvent from a solution involves some form of **distillation**.

When a solution is being dealt with in which only the solvent is volatile, the process of simple distillation will serve for the recovery of the solvent in an almost pure state. If, however, the solution consists of a mixture of volatile liquids whose boiling points are not very far apart (say less than  $60^{\circ}$ ), **fractional distillation** is necessary in order to separate them. This process has been described in Chapter 3 (page 50).

It must be noted, however, that some substances of widely differing boiling points form **constant boiling mixtures** which distil unchanged in composition and at a constant temperature (provided that the pressure is unchanged). Thus, a mixture of hydrogen chloride and water behaves in this way (cf. page 539). At 760 mm. pressure solutions containing 20.24 per cent of hydrogen chloride distil at  $110^{\circ}$  C. without any change in composition. More, or less, concentrated solutions, when heated, lose hydrogen chloride or water, respectively, until the residue attains this composition, when the constant boiling mixture distils over.

### § 11 Solutions of Gases in Solids

Many examples are known of gases being taken up by solids, such as the action of hydrogen on palladium and the ability of charcoal to absorb many gases (see pages 292, 357). There are different ways in which this may occur, not all of which are correctly described as solution. Most of the cases of gases being taken up by solids are examples of adsorption (pages 292, 358), which is a surface effect, but instances are known of the true solution of gases in metals and these phenomena are of industrial importance as they may affect the soundness of castings. A good example is furnished by the case of copper and hydrogen. The solubility of the hydrogen increases with rise of temperature up to the melting point at which it is 2 c.c. per 100 gm. of copper at 760 mm. Hydrogen is also soluble in solid nickel, 100 gm. of which dissolve 8.16 c.c. of the gas at  $822^{\circ}$  C. and 9.75 c.c. at  $923^{\circ}$  C. (at 764 mm.).



## § 12 Solubility of Gases in Liquids

Gases, like solids and liquids, are found to vary enormously in the extent of their solubility in liquids such as water. Thus, for example, one volume of water, at standard temperature and pressure, will dissolve 1200 volumes of ammonia, and but 0.021 volume of hydrogen.

In this respect the solubility relations of gases stand in sharp contrast to their behaviour in other circumstances for no "common" solubility has been observed, and we have no generalization of such wide applicability as Boyle's and Charles's Laws.

For a given gas, however, regularities are observed in the effect of pressure and temperature on solubility, particularly the former.

**The influence of pressure** on the solubility of gases which are not very soluble in water is summed up in **Henry's Law** which states that: **the mass of a gas dissolved by a given volume of a liquid at a given temperature is proportional to the pressure.** Since according to Boyle's Law the volume of a given mass of gas is inversely proportional to the pressure, the law may also be stated in the form: **the volume of a given gas dissolved by a given volume of a liquid is independent of the pressure.**

This law thus describes the behaviour of the less soluble gases very well—carbon monoxide, nitrogen, hydrogen, oxygen—but not the more soluble gases like ammonia, hydrogen chloride, sulphur dioxide. The deviation is not very great with carbon dioxide, though it is appreciable. Henry's Law refers (1) to gases which do not act chemically on the solvent. When carbon dioxide dissolves in water, one portion enters into combination to produce a new substance—carbonic acid—while the other portion dissolves in the physical sense as carbon dioxide. The latter portion alone comes within the province of Henry's Law. Henry's Law also assumes (2) that the molecules of the dissolved gas are no heavier than the molecules of the gas itself. Hence it may be inferred that if a gas "obeys" Henry's Law, it will have the same **molecular weight in solution and in the gaseous condition.** Henry's Law is therefore to be regarded as a link connecting the molecular weights of gaseous and dissolved substances with one unit of measurement.

### The Influence of Temperature

The solubility of a gas in a liquid is very sensitive to changes of temperature. The higher the temperature, the less the solubility of the gas.

This is illustrated by the curve (Fig. 13.6) which shows the solubility of chlorine at various temperatures. The solubility of gases always *diminishes* with temperature (which is the reverse of the behaviour of most solids).

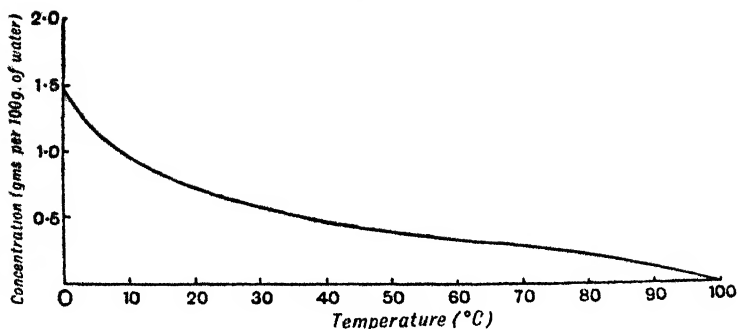


Fig. 13.6.—Solubility of Chlorine

### § 13 Determination of the Solubility of a Gas in a Liquid

The solubility of gases in a liquid can be conveniently determined in the following apparatus, modified from that used by R. Heidenhain and I. Meyer

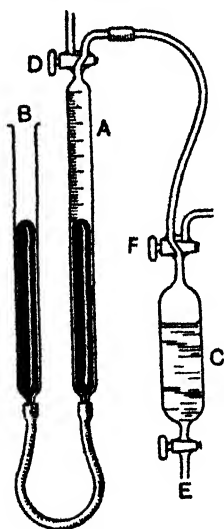


FIG. 13.7.  
Determination of the  
Solubility of Gases

(1863). The pipette *C* (Fig. 13.7) is filled with a measured volume of the solvent, e.g., water previously boiled to expel dissolved air. It is connected with a Hempel's burette by means of a piece of thick-walled rubber tubing of narrow bore. Before using the apparatus the volume of the pipette *C* between the two taps *D* and *E* must be determined. For investigating the solubility of gases such as carbon dioxide a suitable volume for the pipette is 100 ml; for less soluble gases a pipette of larger volume should be used. During an experiment the pipette is immersed in a thermostat. The gas under investigation is introduced into the measuring tube *A*, via the three-way cock *D*, by first raising and then lowering the levelling tube *B*. A definite volume of liquid is then run from the pipette *C* by opening the lower cock *E* and putting the pipette *C* in communication with the burette by means of the cocks *D* and *F*. The weight of the water run out is found so that the weight (and volume) of water remaining in the pipette is known. A certain amount of gas enters the pipette. The contents of the pipette are then agitated, and when all is in equilibrium and the liquid is saturated and the mercury in the burette and levelling tube are at a constant level, the lower end of the absorption pipette is placed beneath a vessel of mercury, and the liquid in the pipette is brought to its former level. The diminution of the volume of gas in the burette represents the volume of gas absorbed by the volume of liquid in the pipette at the temperature and barometric pressure at the time of the experiment.

The results are usually expressed as the number of volumes of gas reduced to S.T.P. absorbed by one volume of liquid. This has also been called by Bunsen the *absorption coefficient*.

### § 14 The Solubility of Mixed Gases

When a mixture of two gases is exposed to the action of a solvent, the quantity of each gas dissolved by the liquid depends upon the volume and the solubility of each gas present. The volume of each gas determines its partial pressure, and since the partial pressure of each gas is independent of the others, it follows that **when a mixture of gases is exposed to the action of a solvent, the volume of each gas which is dissolved by the solvent is proportional to its partial pressure.** Each gas behaves as if the others were absent. This is **Dalton's Law**. It is a simple extension of Henry's Law.

An interesting and important example of this principle is its application to the dissolving of atmospheric air in water. As we shall see in Chapter 26, air consists of nitrogen, oxygen, water vapour, carbon dioxide and small quantities of inert gases. These last may be neglected for the moment.

When air containing, say, 79 volumes of nitrogen and 21 volumes of oxygen, and 0.04 volume of carbon dioxide, is shaken up with water, the volume of each gas absorbed by the water can be approximately computed in the following manner: The relative solubilities are: nitrogen, 0.02; oxygen, 0.04; and carbon dioxide, 1.79. The partial pressure of each gas is proportional to the relative volume of that gas present in a given volume of air. If the pressure of air be just one atmosphere, the partial pressure of the nitrogen will be proportional to  $0.79 \times 1$ ; of oxygen,  $0.21 \times 1$ ; and of carbon dioxide,  $0.0004 \times 1$ . Hence the relative volumes of these gases absorbed by the water will be: nitrogen,  $0.79 \times 0.02 = 0.0158$ ; oxygen,  $0.21 \times 0.04 = 0.0084$ ; and carbon dioxide,  $0.0004 \times 1.79 = 0.00072$ . Hence 1 c.c. of water dissolves 0.0158 c.c. of nitrogen; 0.0084 c.c. of oxygen; and 0.00072 c.c. of carbon dioxide. The composition of the dissolved gases, if removed from the air by boiling, or exposure to a vacuum, will therefore be: nitrogen, 63.9 per cent; oxygen, 33.2 per cent; carbon dioxide, 2.9 per cent. The relatively large solubility of carbon dioxide is counterbalanced by its low partial pressure, otherwise we might expect a heavy rain-storm to remove a great part of the carbon dioxide from the atmosphere.

### § 15 Solutions of Gases in Gases

Gases, as we have seen, are completely miscible in all proportions, providing there is no chemical action, and these mixtures may be considered to be solutions of one gas in another. They correspond in one sense to the completely miscible liquids referred to in § 8. The general behaviour of such mixtures has been considered in Chapter 3, where it was seen (page 27) that, so long as there is no chemical action between them, each gas in a mixture behaves independently of the others present. The behaviour of a mixture of gases towards a liquid

solvent like water, which was considered in the preceding section, is an example of this.

An important part of the study of mixed gases concerns means for separating them. Among these may be mentioned the methods depending upon:

- (i) diffusion;
- (ii) liquefaction;
- (iii) solubility in liquids;
- (iv) chemical methods.

Separation of gases by diffusion has been mentioned in Chapter 3 and is referred to as a means of separating the isotopes of neon (page 34) and of uranium, and the separation of liquid air by fractional distillation has been fully discussed (page 50). Further applications of this method will be mentioned in describing the separation of the Inert Gases (Chapter 26). The removal of ammonia from the unchanged nitrogen and hydrogen in the Haber process (page 430) is another example.

The differential solubility of the gases of the atmosphere results in "air" which has been dissolved in water being richer in oxygen than ordinary air (see § 14 above). Mallet proposed to separate oxygen from atmospheric air in this way. If the carbon dioxide be removed by passing the air through an aqueous solution of sodium hydroxide, the oxygen and nitrogen in the remaining gases after the first absorption will be nearly in the proportion: nitrogen 65.7 per cent, and oxygen 34.3 per cent. If this mixture be driven from the water by boiling, and the mixture again treated with air-free water, a gaseous mixture containing 49 per cent of oxygen is obtained; and after the eighth absorption, a gas containing 98 per cent of oxygen results. The method is not practicable, though it is an interesting application of Henry's and Dalton's Laws.

The separation of gases by chemical means is used in gas analysis. (Cf. pages 118, 586.) Thus carbon dioxide is removed from admixture with other gases by means of concentrated potassium hydroxide solution, and nitric oxide by means of ferrous sulphate solution. In these cases the gas removed can be recovered, and so a true separation is effected. Sometimes the gas removed chemically cannot be recovered directly; for example, oxygen removed by alkaline pyrogallol, or nitrogen by heated magnesium or calcium carbide. (Cf. page 590.)

## § 16 Crystals

A solid homogeneous substance may exist as an amorphous body or as a crystalline one, and in the great majority of cases solid substances are found to be made up of aggregates of **crystals**.

A crystal in this sense is a solid which has a definite geometrical shape, with flat faces and sharp edges. A solid which has no definite shape and which cannot be obtained in the form of crystals is called

amorphous. Many substances, however, which were once thought to be amorphous, are now known to be made up of exceedingly small crystals, and glass, which is often described as an amorphous solid, is more accurately referred to as a super-cooled liquid. Glass itself sometimes crystallizes (e.g., when old glass is heated); it is then said to have devitrified. (Cf. page 779.) Flint is usually called an amorphous form of silica. **Every crystalline substance of definite chemical composition has a specific crystalline form characteristic of that substance.** This is sometimes called **R. J. Haüy's Law**. The faces of crystals of the same substance may vary in size and shape; but if the crystals possess the same chemical composition, and are at the same temperature, the interfacial angles have the same numerical value. In other words, **the angles between similar faces of crystals of the same substance are precisely the same, and are characteristic of that substance.** This "law" was first announced by D. Guglielmini (1688). This means that the crystalline form of a substance is not determined by the absolute position nor by the sizes of the faces of the crystal, but rather by the dimensions of the interfacial angles. The primary dominant faces, so to speak, may persist while the angles and edges of some of the crystals may be truncated and bevelled, giving rise to new facets. In spite of these variations, the crystals of a given substance always retain its fundamental form. Different substances may have a similar chemical composition and different interfacial angles.

This is an essential property of crystals.

Another characteristic property of crystals is that of cleavage. Many crystals tend to split along certain definite directions or planes which are called cleavage planes. These planes may be parallel to the faces of the original crystal, but sometimes they are not. An interesting example of the application of this property of cleavage is in the "cutting" of diamonds. Diamonds are intensely hard but can be split along the natural cleavage planes of the crystal. This property of cleavage has had an important bearing on the development of our knowledge of crystal structure.

### § 17 The Classification of Crystals

The great variety of crystals formed by different substances, each substance having a characteristic crystalline form or forms (characterized by the interfacial angles), have been classified into *seven systems* and *thirty-two types*. The study of these is a special branch of science known as *crystallography*, and it is only possible here to indicate the general principles on which it is based.

Certain qualities are peculiar to the members of each of the seven systems into which the great variety of crystals can be arranged. For instance, the planes of symmetry of each class are characteristic. A **plane of symmetry** is an imaginary plane which divides the crystal into two parts such that one part is the exact but inverse counterpart

of the other. In other words, the two parts bear to one another the same relation that the image in a mirror bears to its object. The mirror is the equivalent of a plane of symmetry. A crystal of sodium chloride, for example, has nine planes of symmetry; three are indicated in Fig. 13.8, and six others are obtained by taking planes diagonally through three faces of the cube. The crystal of gypsum, Fig. 13.9, has only one plane of symmetry; and a crystal of zinc sulphate has three planes of symmetry, Fig. 13.10.

#### Planes of Symmetry

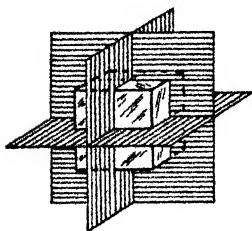


FIG. 13.8  
Sodium Chloride

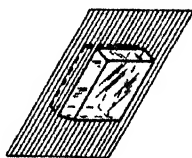


FIG. 13.9.  
Gypsum

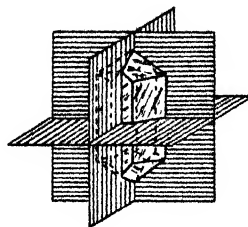


FIG. 13.10.  
Zinc Sulphate

Then again, a crystal may be rotated about a definite axis through an angle, such that the faces, edges, and corners are brought into similar or symmetrical positions, and the aspect of the crystal is the same as before rotation. The axes of rotation are then called axes of symmetry. Thus we speak of dyad, triad, tetrad, and hexad axes of symmetry according as there are 2, 3, 4, or 6 positions of symmetry during a complete rotation. Thus Fig. 13.11, *A*, represents a horizontal cross-section of a crystal with one hexad axis of symmetry, because during the rotation of the crystal about the axis *O*, there are six positions where the original aspect of the crystal is the same. Fig. 13.11, *B*, *C*, *D* respectively, denote tetrad, triad, and dyad axes of symmetry.

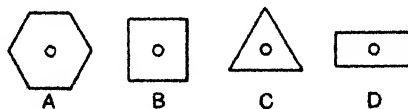


FIG. 13.11.—Axes of Symmetry

The classification of crystals is thus determined by their symmetry and not by the particular external form of a given crystal. The names of the seven systems, together with some of their characteristics and the names of representative examples of each type, are given below, and a series of photographs of real crystals of each type is given in Plates 5 to 11.

**I. Triclinic system.**—Crystals of this system have no axes nor planes of symmetry. This system has also been designated the "anorthic," "clino-rhomboidal," "asymmetric," or the "double oblique" system.

**EXAMPLES.**—Potassium dichromate; copper sulphate— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; calcium thiosulphate— $\text{CaS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ ; boric acid; potassium ferricyanide; anhydrous manganese sulphate; copper selenate; anorthite—lime felspar; cryolite; etc.

**II. Monoclinic system.**—Members of this system have one plane of symmetry, or one dyad axis of symmetry, or both a plane and dyad axis. This system has also been styled the "monosymmetric," "clino-rhombic," or the "oblique" system.

**EXAMPLES.**—Borax— $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ; gypsum; ferrous sulphate— $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; sodium carbonate— $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ; felspar—orthoclase; sodium sulphate— $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; ammonium magnesium sulphate— $(\text{NH}_4)_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ; potassium chlorate; potassium tetrathionate— $\text{K}_2\text{S}_4\text{O}_8$ ; tartaric acid; sulphur—from fusion; cane sugar; arsenic disulphide—realgar; etc.

**III. Rhombic system.**—Here the crystals may have three planes of symmetry, and three dyad axes of symmetry. This system is sometimes called the "orthorhombic," "trimetric," or the "prismatic" system.

**EXAMPLES.**—Zinc sulphate— $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ; magnesium sulphate— $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; ammonium magnesium phosphate— $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ; potassium sulphate; aragonite; anhydrous sodium or silver sulphate; sulphur from solution; barytes; sodium arsenate; sodium phosphate— $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ; iodine; potassium nitrate; tartar emetic; potassium permanganate; topaz; marcasite; tin; tridymite; silver nitrate; lead carbonate; silver sulphide.

**IV. Tetragonal system.**—The members of this system may have five planes of symmetry, one tetrad, and maybe four dyad axes of symmetry. This system is sometimes called the "pyramidal," "quadratic," or the "quaternary" system.

**EXAMPLES.**—Rutile; cassiterite; zircon; mercurous chloride; potassium ferrocyanide; nickel sulphate; potassium hydrogen phosphate— $\text{KH}_2\text{PO}_4$ ; native lead molybdate— $\text{PbMoO}_4$ ; sodium meta-antimonite— $\text{NaSbO}_3$ ; potassium hydrogen arsenate— $\text{KH}_2\text{AsO}_4$ ; scheelite, tin; strychnine sulphate; etc.

**V. Trigonal system.**—The crystals of this system may have three planes of symmetry, one triad, and three dyad axes of symmetry. This system is sometimes called the "rhombohedral" system, and it is sometimes regarded as a special development of the hexagonal system.

**EXAMPLES.**—Sodium periodate— $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ ; quartz; tourmaline; antimony; bismuth; calcite; ice; graphite; sodium nitrate; arsenic; nickel sulphide—millerite; cinnabar; calcium chloride— $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ; corundum; cadmium carbonate; bismuth iodide; ferrous carbonate, zinc carbonate; manganese carbonate; etc.

**VI. Hexagonal system.**—Here the crystals may have seven planes of symmetry, one hexad, and six dyad axes of symmetry.

**EXAMPLES.**—Beryl; apatite; cadmium sulphide—greenockite; copper sulphide; lead iodide; magnesium; beryllium; zinc; cadmium; calcium; pyrrhotite; etc.

**VII. Cubic system.**—The crystals in this system may have nine planes of symmetry, six dyad, three tetrad, and four triad axes of symmetry. This system has been variously styled the "isometric," "regular," "tesseral," "octahedral," or the "tessural" system.

**EXAMPLES.**—Diamond; potassium chloride; sodium chloride; alum; fluor-spar; iron pyrites; lead nitrate; magnetic oxide of iron; barium nitrate; arsenic trioxide; galena; garnet; ammonium chloroplatinate; silver chloride; boracite; iron; platinum; lead; phosphorus, gold, copper, silver; arsenic; etc.

### § 18 The Internal Structure of Crystals

Crystals are not only peculiar in the regularity of their external shape, but they also possess a definite internal structure. The properties of crystals are not always the same in different directions. The hardness, elasticity, crushing strength, rate of solution in acids, optical, thermal, and electrical properties are generally different in different directions. This means that the elasticity, refraction of light, thermal expansion, etc., of a crystal is usually different when measured in different directions. The external form of crystals is their most obtrusive characteristic, and it was naturally the first to arrest attention; but the geometrical shape is by no means the most characteristic property of crystals, because the external geometrical form may be destroyed, and yet the fragments do not cease to be crystals. On the contrary, the most perfect glass model of a crystal is not a crystal, because it lacks the characteristic internal properties of crystals.\*

It is clear, as has been long realized, that the structure of crystals can be explained on the supposition that a crystal is an aggregate of particles arranged in space in an orderly manner. But such a vague generalization does not take us very far. Haüy in 1784 showed that simple geometrically shaped solids such as spheres or cubes could be piled up in such a way as to reproduce many crystal forms, thus showing that the regular piling of units could produce shapes analogous to those of actual crystals.

Bravais in 1848 modified and extended this idea by supposing that the solid "units" of Haüy's models were replaced by small particles situated at the centres of the geometrically shaped solids. In this way there results an open structure of small particles arranged in a lattice—such an arrangement being called a **space lattice**. We may further define a space-lattice as an arrangement of rows of points in three dimensions, in such a way as to form a series of cells, all consisting of parallelepipeds. A simple space-lattice and the corresponding Haüy's model are illustrated in Figs. 13.12 and 13.13.

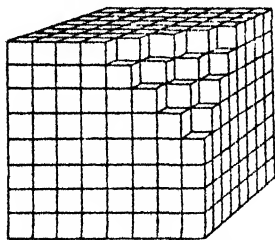


FIG. 13.12.—Haüy Model

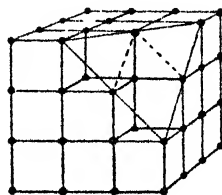
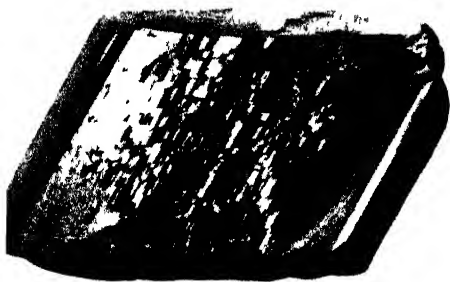


FIG. 13.13.—Space-lattice

\* The shapes of gems cut and polished to accentuate the ornamental value of the gem must not be confounded with crystal structure. Similarly, the term "crystal" applied to cut glass has a different meaning from the special use of the word "crystal" in the text. Transparent glass is not crystalline; some varieties of opaque glass are more or less crystalline.





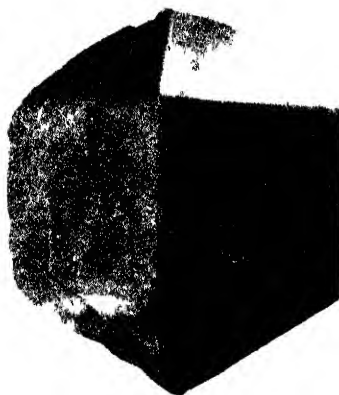
5 Copper sulphate *Triclinic system*



6 Orthoclase *Monoclinic system*



7 Barites *Rhombic system*



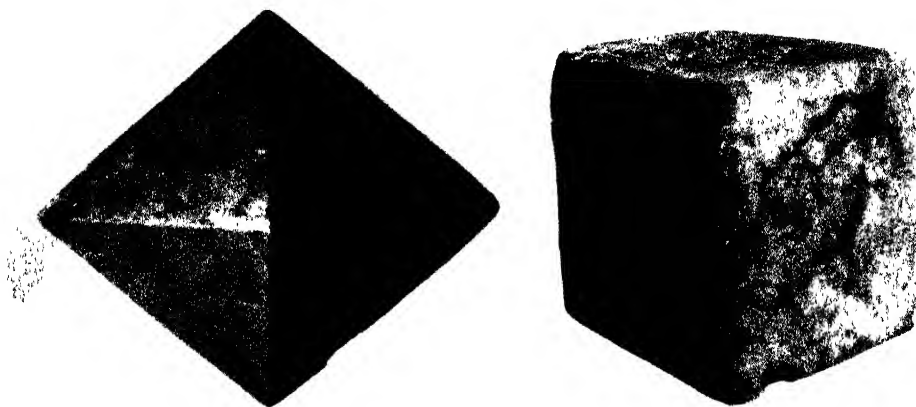
8 Zircon *Tetragonal system*



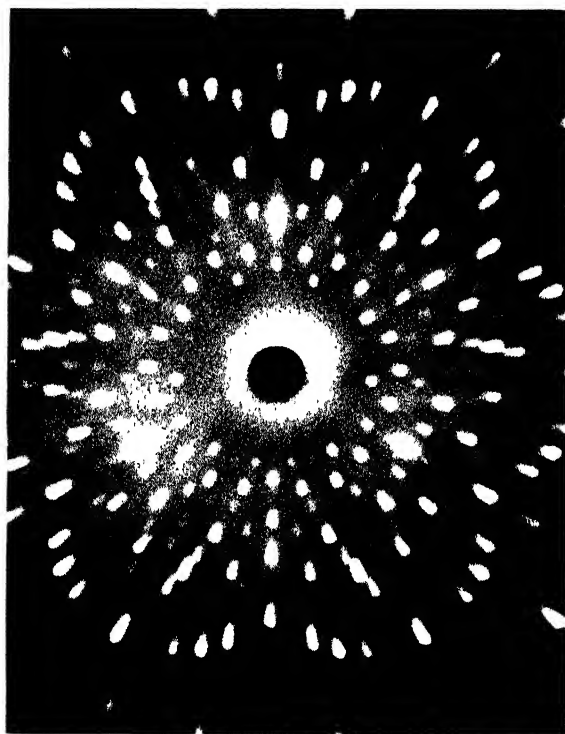
9 Calcite *Trigonal system*



10 Apatite *Hexagonal system*



11 Fluorspar and pyrites *Cubic system*



12. Laue photograph of quartz

The work of Bravais and others has shown that 230 different space-lattices are theoretically possible, and that these will account for all the thirty-two classes (and seven systems) of crystals as ordinarily classified. It was further established that all the patterns of crystal faces found in actual substances could be explained on the assumption that all the crystals of any one system were constructed from space-lattices having the symmetry characteristic of that system.

## § 19 X-rays and Crystal Structure

The theory of crystal structure based on the idea of the space-lattice was worked out long before any means had been found for obtaining *direct* evidence for the internal structure of crystals. The application of X-rays to the problem by von Laue and by Friedrich and Knipping in 1912 was the first step towards the solution of this problem.

In Chapter 10 (page 136) it was pointed out that this work gave the first *direct* evidence of the nature of X-rays; it also resulted in our being able to determine the internal structure of a great many crystalline substances.

The phenomenon of diffraction is dealt with fully in text-books of physics, in which it is shown that when a beam of light strikes a series of very fine lines ruled regularly on the surface of a metal or glass plate, each line acts as a fresh source from which a secondary train of light waves spreads out, or is, as we say, diffracted. These diffracted rays "interfere" both with each other and with the original rays, causing enhancement of the light waves along certain definite directions. This principle is made use of in determining the wave-length of ordinary light by means of "diffraction gratings."

Now if the space-lattice theory of crystal structure be correct, the various planes of particles in the crystals should act in an analogous way upon light of sufficiently short wave-length. This was shown to be the case by the experiments of Laue, Friedrich and Knipping, who passed a pencil of X-rays through a suitable crystal and then allowed it to fall on a photographic plate.

Plate 12 illustrates the result of one such experiment; the black central spot caused by the undeviated beam of X-rays being surrounded by a pattern of spots which were easily shown to be characteristic of the type of crystal being used.

This process was modified by W. H. and W. L. Bragg, by using the crystal as a reflection grating instead of passing the beam of X-rays through the crystal.

Fig. 13.14 illustrates the principle of the Bragg method.  $PA$  and  $PA'$  represent incident and "reflected" rays from a point in the topmost lattice plane  $CD$  of a crystal.  $EF$  and  $GH$  are two similar planes lower down in the crystal, the distance between successive planes being  $d$ .  $QB$  and  $QB'$  are incident and "reflected" rays which have been diffracted in the second lattice plane. It can easily be seen that the difference in the lengths of the paths traversed by  $APA'$  and  $BQB'$  is  $RQ + QS = 2PQ \sin \theta = 2d \sin \theta$ . These two rays will interfere and reinforce each other when this difference in path is equal to an integral number of wave-lengths; i.e., when

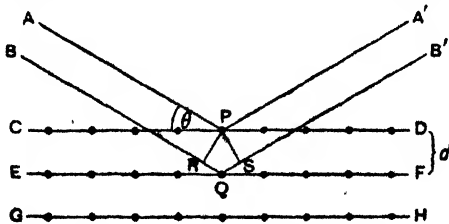


FIG. 13.14 — Reflection of X-rays from a Crystal

where  $\lambda$  = wave-length of the X-rays used and  $n$  is a small integer. By this means, therefore, the distances between the planes in crystals can be compared and measured

$$n\lambda = 2d \sin \theta$$

For a full discussion of the way in which the results of experiments based on

these principles have been used for the elucidation of the details of crystal structures suitable works on physical chemistry or on the X-ray analysis of crystals must be consulted; but a summary of some of the conclusions is given below.

In the first place, the mathematically deduced space-lattice theory has been completely confirmed; and, in addition, a great deal of information has been obtained as to the mode of combination of many compounds.

In the case of rock salt, for example, it soon became clear that the units from which the lattice is built up are not actual molecules of sodium chloride, but atoms (or more probably ions—see Chapter 15, page 216) of sodium and chlorine. This result followed from evidence which showed that in certain directions in the crystal the planes (actually the octahedral plane) of the space-lattice consisted of particles all of the same kind in a given plane, but alternately of different kinds

as we pass from plane to plane. To sum up, the rock-salt crystal was shown to have the structure represented in Fig. 13.15.

The remarkable conclusion is thus forced on us that in such a crystal a given sodium atom is not united to any particular chlorine atom—the identity of a particular molecule is lost.

Similar results attended the investigation of other crystals; but in such a substance as calcium carbonate it was found that calcium ions and  $\text{CO}_3$  groups constituted the units from which the crystal lattice is built up.

Crystals of salts (which are electrolytes—cf. Chapter 15) usually have lattices made up of individual ions, as in the case of rock salt or calcium carbonate.

These are substances which are held together by electrovalent links, as explained in the preceding chapter. Compounds whose atoms are united by covalent links are found to have a different type of unit making up the lattice. Two types have been distinguished, viz., that in which the unit is the molecule, and that in which the crystal is a kind of giant molecule.

The first is the most usual type, and since a molecule whose atoms are, of course, covalently linked, would not be expected to show very great attraction for similar molecules, we should expect the crystals to be much softer and more readily fusible than those of salts where the units are held together by powerful electrostatic forces. This is, in fact, the case: crystals of covalent compounds such as benzene and sulphur are much softer and melt at a much lower temperature than those of salts like sodium chloride.

In the giant molecule type of crystal every atom is chemically combined by a covalent linkage to the next. Examples of this type are the diamond (the internal structure of which is illustrated in Fig. 22.3, page 368) and aluminium oxide after ignition. It would be expected that crystals built up on this kind of plan would be hard and very difficult to fuse, and the examples quoted confirm this expectation.

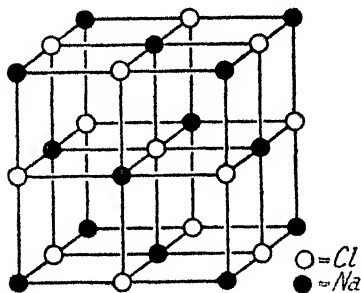


FIG 13.15.—Structure of Rock-salt Crystal

## CHAPTER 14

# PROPERTIES OF DILUTE SOLUTIONS

The act of dissolution is probably not due to chemical combination in the first place, but is probably analogous to the sublimation of a solid into a gas, and proceeds from the detachment of molecules from the surface of the solid, and their intermixture with those of the surrounding liquid. This is doubtless due to the impact of the moving molecules of the liquid.—W. G. TILDEN.

The substitution of analogy for fact is the bane of chemical philosophy; the legitimate use of analogy is to connect facts together and to guide to new experiments.—H. DAVY.

Vague similarities in certain properties are never sufficient to determine a person who earnestly seeks for the truth and is not shackled by hypotheses.—J. BERGMAN.

### § 1 Diffusion in Liquids

LET a large crystal of a coloured salt—say copper sulphate—be placed at the bottom of a tall glass cylinder, and the remainder of the jar be filled with water. The coloured salt is chosen because the movements of the resulting solution can be readily seen. Let the jar stand where it will not be disturbed by evaporation, agitation, etc. The surface of separation between the solid and solvent will be gradually obliterated; in time, the coloured salt will diffuse uniformly throughout the whole body of liquid. The diffusion of the salt in the solvent seems to be analogous with the process of diffusion in gases, and so it is inferred that the molecules of the liquid are in perpetual motion in all directions; and that the protracted time occupied by the diffusion of the molecules of the dissolved salt in the liquid is a consequence of the close packing of the molecules of the liquid.

Just as the molecules of a gas in a closed vessel are disseminated in a relatively large space, so are the molecules of a solid in solution scattered in a relatively large volume of solvent. It is true that the molecules of the salt in solution could not occupy the space if the solvent were absent, otherwise the analogy between a substance dissolved in a solvent and a gas scattered in space would be very close.

If the diffusion of gases be resisted by placing a permeable partition between two gases, a pressure will be exerted upon the partition (see page 21). It is easy to show that the particles of a dissolved substance exert a similar pressure when a partition is placed between the solution and solvent so that the partition offers no obstacle to the free circulation of the molecules of the solvent, but resists the free passage of the molecules of the dissolved substances.

A piece of the thinnest grade of commercial cellophane, about 10 cm. square, is folded over the end of a wide glass tube and bound tightly with string. The cellophane and the string are then immersed in

water, when the cellophane softens and the string contracts, so making a water-tight joint. A quantity of a concentrated solution of cane sugar is placed in the tube and the whole is immersed in a vessel of water as in Fig. 14.1. The level of the solution in the tube is marked with gummed paper and the apparatus is allowed to stand overnight. In the morning the liquid in the tube will have risen by several centimetres. Water has obviously passed through the membrane into the sugar solution.

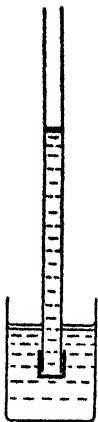


FIG. 14.1.  
Illustration of  
Osmotic Pressure

The passage of water through a membrane in this manner is called **osmosis**—from the Greek *ὠμός* (*osmos*), a push. The membrane permeable to the solvent, impermeable to the dissolved substance, is called a **semipermeable membrane**. The extra pressure exerted upon the membrane by the sugar solution was styled, by W. Pfeffer (1877), "the **osmotic pressure** of the sugar solution." Solutions with the same osmotic pressure are said to be *isosmotic* or *isotonic*.

## § 2 The Measurement of Osmotic Pressure

A cellophane membrane is unsatisfactory when exact measurements are required because, to a certain extent, the results depend upon the nature of the membrane; the cellophane membrane is not strong enough to withstand the great pressures developed by osmosis; and, most serious of all, it is not truly semipermeable, an appreciable amount of, say, sugar does actually pass through the membrane. It would therefore be as profitable to measure the pressure of a gas in a leaking vessel as to try to measure the osmotic pressure of a solution with a membrane which allows part of the dissolved substance to pass through. The most successful membrane is a film of copper ferrocyanide deposited in the walls of a porous pot.

A convenient way of preparing such a membrane (described by P. H. Adie) is to take a clean dry porous pot *A* (Fig. 14.2), fixed on to a wide glass tube *B* by means of sealing-wax. The pot is then lowered into a 3 per cent solution of copper sulphate, and a 3 per cent potassium ferrocyanide solution is poured into the pot. The whole apparatus is now enclosed in a vessel which can be exhausted, and allowed to remain *in vacuo* for several days in order to remove air from the pores of the pot. The pot is then allowed to stand in more dilute solutions at atmospheric pressure for about three weeks. The manometer *C* is attached by sealing it on to the tube *D*,

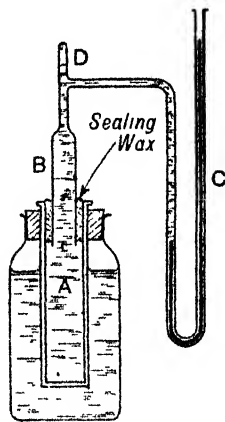


FIG 14.2.  
Measurement of  
Osmotic Pressure

itself joined on to *B*. The solution is introduced through the top of *D*, which is then sealed off

By means of apparatus such as this, Pfeffer obtained results which, although not of the order of accuracy now obtainable, were yet sufficiently accurate to enable Van't Hoff in 1887 to develop a theory of dilute solutions which has been, and is, of the highest importance (see § 3 below)

The technique of the measurement of osmotic pressure with a high degree of accuracy and in concentrated solutions has been developed more recently by Morse and Frazer and their collaborators in America and by Berkeley and Hartley in England

Morse and Frazer (1911) employed in essence Pfeffer's method, using the most elaborate precautions to obtain porous pots of uniform texture and to produce very perfect membranes. For very high pressures they utilized the apparatus shown in Fig 14.3. Their membranes were obtained in the following manner. The cell was filled with a very dilute solution of lithium sulphate and immersed in a similar solution, and an electric current was passed. In this way air was removed from the pores of the cell. After washing it was filled with potassium ferrocyanide solution and placed in a solution of copper sulphate. A platinum cathode was placed inside the pot and a copper anode in the copper sulphate solution. A current was passed so that the copper and ferrocyanide ions were driven towards each other in the walls of the pot.

In Pfeffer's experiments and their own earlier work the solution was placed in the porous pot which was surrounded by solvent. The pressure thus developed inside the pot and was so directed outwards. It can easily be realized that the membrane would be able to withstand a higher pressure in the reverse direction for here the principle of the arch is involved.

The apparatus shown in Fig 14.3 makes use of this principle. The porous pot *A* is firmly clamped inside the bronze cylinder *B* into which the manometer *C* was securely fixed. The solution was placed outside the porous pot (in the walls of which the membrane was deposited) and the pot was kept full of water. By means of this apparatus pressures as high as 273 atmospheres were successfully measured.

The manometer used consisted of a tube containing oil in which a resistance wire was immersed. The electrical resistance of this wire was measured; it was proportional to the pressure exerted on it. In this way very high pressures could be measured without appreciable dilution of the solution occurring.

The method employed by Berkeley and Hartley (1906) was essentially different in that instead of measuring the pressure developed in the cell by the passage of the solvent into it they applied a gradually increasing hydrostatic pressure to the solution until the direction of flow of the solvent was reversed. The value of the pressure at the turning point, that is, of the pressure which is just sufficient to prevent the inward flow of solvent, is taken as the osmotic pressure.

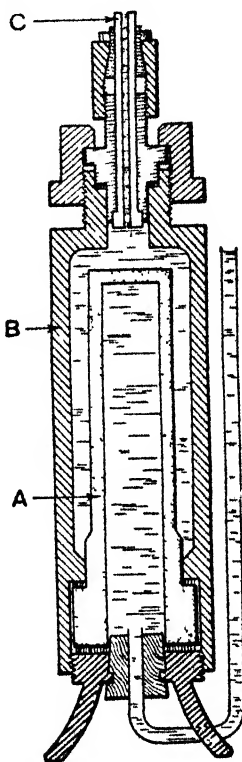


FIG 14.3—Osmotic Pressure Apparatus (Frazer and Myrick)

### § 3 Van't Hoff's Theory of Dilute Solutions

In § 1 of this chapter reference was made to the analogy which seems to exist between the behaviour of gases and the behaviour of substances in solution. After Pfeffer had published the results of his experiments on the determination of osmotic pressure, J. H. van't Hoff developed this analogy very considerably.

Examination of Pfeffer's results showed that (i) the osmotic pressures of different solutions of the same solute are proportional to the concentration of the solutions, at a fixed temperature; and (ii) the osmotic pressure of a solution of fixed concentration is proportional to the absolute temperature. These conclusions were used and developed by J. H. van't Hoff (1885). They may be expressed in the form:

$$\frac{P}{C} = KT$$

where  $P$  = osmotic pressure of the solution

$C$  = concentration of the solution

$T$  = absolute temperature

and  $K$  = a constant.

Since the concentration is inversely proportional to the volume of the solution for a given mass of solute, this may be rewritten:

$$PV = KT$$

where  $V$  = volume of solution in which a given amount of solute is dissolved.

If now in this expression we substitute the values for  $P$  and  $V$ , obtained by experiment at a given temperature ( $V$  being now expressed as the volume of solution containing one gram-molecular weight of solute), we can find the value of  $K$ . Using the results obtained, for example, by Berkeley and Hartley, this gives a value for  $K$  equal to within 1 per cent of the value of the gas constant  $R$ , calculated from the gas equation  $PV = RT$  for the case of a gas (cf. page 26). We are thus justified in writing the equation for a dilute solution in the same form as for a gas: in the case where  $n$  gram-molecules of solute are dissolved in volume  $V$  of solution

$$PV = nRT.$$

J. H. van't Hoff (1885) was able, further, to justify the analogy between the behaviour of gases and solutions on theoretical grounds based upon the laws of thermodynamics and the conception of the semipermeable membrane, and he arrived at the important conclusion that the osmotic pressure of a solution is equal to the pressure which the dissolved substance would exercise in the gaseous state if it then occupied a volume equal to the volume of the solution.

An important deduction from the result expressed in the equation  $PV = nRT$  is that since  $P = \frac{nRT}{V}$  the osmotic pressure is propor-



tional to the number of gram-molecular weights of solute dissolved in a given bulk of solution, or in other words, **equimolecular solutions of all substances have the same osmotic pressure.\*** Osmotic pressure is thus what is called a **colligative** property, that is, a property which depends on the number of particles present and not on the kind of particles. It will thus furnish a method for the determination of molecular weights, and although the manipulative difficulties involved in the accurate measurement of osmotic pressures cause the method to be but rarely used, it provides the theoretical basis, nevertheless, for some of the most important and widely used methods for the determination of molecular weights in solution (see below, §§ 5, 6, 7, 8).

It is, however, important to notice that just as the equation  $PV = RT$  is the equation for a *perfect* gas, to the behaviour of which actual gases conform with different degrees of closeness, none being absolutely exact, so in the application of the corresponding equation to solutions the equation expresses the behaviour of an *ideal* solution to which actual solutions conform more or less. The deviations which occur are probably to be accounted for in a manner similar to that of gases, viz.:

- (i) attraction between the molecules of the solute;
- (ii) attraction between molecules of the solute and solvent,
- (iii) the volume of molecules themselves.

As in the case of gases, the divergence is wider at high concentration (i.e., high pressure and small volume), and the simple Van't Hoff theory is in reality only applicable to *dilute* solutions and within a moderate range of temperature. Also as already indicated, it requires modification when applied to solutions of electrolytes. (Cf. Chapter 15, page 219)

#### § 4 Mechanism of Osmotic Pressure and Membrane Action

The close analogy between the behaviour of dilute solutions and gases demonstrated by Van't Hoff led naturally to the view that osmotic pressure and gas pressure are brought about by similar causes, i.e., to bombardment by the molecules of the solute or gas of the semipermeable membrane or the walls of the containing vessel respectively. At the same time it was natural to assume that the action of the semipermeable membrane is that of an atomic sieve whose pores, while large enough to permit the passage of solvent molecules, are too small to allow of solute molecules passing through them.

These explanations are not now felt to be completely satisfactory as they stand, particularly as it has been shown that the actual pore-diameter of a copper ferrocyanide membrane is too large to block the passage of even a sugar molecule. This has led to various modifications in the theory, such as the suggestion that the pores are hydrated (or solvated) to an extent sufficient to prevent the passage of solute molecules.

Another view visualizes the membrane as being composed of very fine capillaries of very small diameter; so small that the whole capillary is under the influence of surface forces. On this theory the semi-permeability of the membrane is accounted for by supposing that the copper ferrocyanide adsorbs water but not sucrose. There would thus be free passage for the former but not the latter.

The favoured explanation, at present, is that which supposes that the membrane exerts preferential solubility; it is permeable to those substances which will dissolve in it and impermeable to those which will not. This view is in accord with

\* This statement is only true for solutions of non-electrolytes. The corresponding behaviour of electrolytes is discussed in Chapter 15.

the behaviour of non-aqueous solvents in contact with other membranes (e.g. pyridine or acetone solutions and vulcanized rubber) whereas the adsorption theory is not.

In any case, the driving force which brings about osmosis is the difference in vapour pressure between the solvent and solution; equilibrium can only be established when the pressure exerted externally on the latter is equal to the difference between the vapour pressures of solvent and solution.

### § 5 Molecular Weight of Dissolved Substances

Van't Hoff's Theory of Solution gives, in theory, a means of measuring molecular weights in solution by finding the osmotic pressure of a solution of known concentration, but, as explained in § 3, this method is not practicable in most cases. However, a close relation does exist between the osmotic pressure of a solution and the lowering of the vapour pressure as compared with that of the pure solvent, and between this lowering of the vapour pressure and the depression of the freezing point, and the elevation of the boiling point, of a solution. These latter changes provide important and widely used methods for the determination of molecular weights.

### § 6 Relation of Osmotic Pressure to the Vapour Pressure of a Solution

M. Faraday knew, in 1822, that the vapour pressure of a solution is lower than the vapour pressure of the pure solvent; but A. Wullner discovered the important fact experimentally, in 1858, that the lowering of the vapour pressure of a solution is proportional to the quantity of substance in solution provided that the dissolved substance is non-volatile. This is sometimes called Wullner's Law.

Suppose a solution *A*, Fig. 14.4, confined in a long-stemmed tube, as illustrated in the diagram, to be separated by a semipermeable membrane *M* from the pure solvent. Let all be confined in a closed vessel. Osmotic pressure will force the solution to rise in the narrow tube to a height *h*, when the whole system is in equilibrium. Let  $p_s$  denote the vapour pressure of the solution in the narrow tube, and  $p$  the vapour pressure of the solvent in the outer vessel. The vapour pressure of the solution at the surface in the narrow tube must be equal to the vapour pressure of the solvent at the same level, otherwise distillation would take place either to or from the surface of the liquid in the narrow tube and there would be a constant flow of liquid respectively to or from the vessel *A* through the semipermeable membrane in order that *h* may have a constant value. Hence, the vapour pressure of solution and solvent at the upper level of the solution in the narrow tube must be the same. The vapour pressure of the solvent at the level *a* will be equal to the vapour pressure of the solvent at the lower level *b* less the pressure of a column of the height *h* or  $p = p_s + w$ , where  $w$  = the pressure of a column of vapour of height *h*. Since the height *h* is determined by the osmotic pressure, which in turn is determined by the

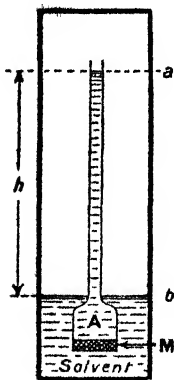


FIG. 14.4

concentration of the solution, there must be a simple proportionality between the osmotic pressure or concentration of the solution and the lowering of the vapour pressure.

This relation is calculated as follows. We have seen that

$$\begin{aligned} p - p_s &= h \times \text{density of vapour} \\ &= h\rho \text{ (say)} \end{aligned}$$

Now, if the vapour be assumed to obey the gas laws, then one gram-molecule of the vapour at a pressure  $p$  and absolute temperature  $T$  will occupy a volume  $v$  given by:

$$\begin{aligned} v &= \frac{RT}{p} \\ \therefore \rho &= \frac{M}{v} = \frac{Mp}{RT} \end{aligned}$$

where  $M$  is the molecular weight of the solvent in the vapour state.

Substituting the value of  $\rho$  in the equation above, we have:

$$p - p_s = h \frac{Mp}{RT}$$

Now the osmotic pressure of the solution is equal to the hydrostatic pressure of the column of liquid of height  $h$ , so that  $P = hs$ , where  $s$  is the density of the solution, which for a *dilute* solution may be taken to be the same as that of the solvent

Substituting the value for  $h = \frac{P}{s}$  in the preceding equation, we now have:

$$\begin{aligned} p - p_s &= \frac{PMp}{RTs} \\ \text{or } \frac{p - p_s}{p} &= \frac{PM}{RTs} \end{aligned}$$

which gives us the relation between the relative lowering of the vapour pressure and the osmotic pressure of a solution

For a given solvent, at a particular temperature,  $\frac{M}{RTs}$  will be a constant, so that the relative lowering of the vapour pressure is proportional to the osmotic pressure.

This relation clearly furnishes, at least in theory, a means for molecular weight determination since the osmotic pressure of a solution of given concentration is inversely proportional to the molecular weight of the solute as we have seen.

This method for determining the molecular weight of a substance from direct measurements of the lowering of the vapour pressure is of great theoretical interest, but in practice the method is seldom employed, because some of the related properties of solutions are more amenable to accurate measurement.

## § 7 Relation of Lowering of Vapour Pressure to the Boiling Point and Freezing Point of a Solution

In the previous chapter (page 184) it was pointed out that Blagden in 1788 detected a relationship between the freezing point of a solution and its concentration. This observation was extended by Raoult (1883-4), who investigated both the depression of the freezing point and the elevation of the boiling point of a solvent owing to the presence of a dissolved substance. As a result of his experiments, he concluded that for solutions of non-electrolytes the depression of the freezing point (or the rise in the boiling point) of a solvent is proportional to the number of molecules of the dissolved substance, and inversely

**proportional to the total number of molecules present.** Expressed in symbols, Raoult's Law is

$$\delta = k \cdot \frac{n}{n + N}$$

where  $\delta$  = depression of the freezing point (or elevation of the boiling point) of a solvent by the presence of a solute

$n$  = number of molecules of solute present

$N$  = number of molecules of solvent present

and  $k$  is a constant.

This important generalization was deduced empirically by Raoult, but can now be seen to have a theoretical basis. For the elevation of the boiling point, or lowering of the freezing point, are clearly related to the relative lowering of the vapour pressure of the solution, and from this Raoult's Law can be deduced mathematically.

The relative lowering of the vapour pressure of a solution is proportional to the osmotic pressure and hence, as we have seen, inversely proportional to the molecular weight of the solute. The boiling point of a liquid is the temperature at which the vapour pressure becomes equal to the pressure of the atmosphere; while the freezing point of a solution is that temperature at which the vapour pressure of the solid solvent and liquid solvent are equal. Hence it follows that the elevation of the boiling point and depression of the freezing point of a solution of given strength are inversely proportional to the molecular weight of the dissolved substance.

Expressed in another way, we may say that one gram-molecular weight of any solute dissolved in a given weight (usually 1000 grams) of solvent depresses the freezing point (or elevates the boiling point) by a constant amount characteristic of the solvent in question. This quantity (represented by  $K$ ) is known as the *freezing* (or *boiling*) *point constant* or the *molecular depression* (or *elevation*) of the solvent.

If now  $w$  grams of a solute of molecular weight  $M$  be dissolved in  $W$  grams of a solvent whose molecular depression (or elevation) is  $K$ ,  $M$  grams of solute dissolved in 1000 grams of solvent\* depress the freezing (or elevate the boiling) point by  $K^\circ$ .

$\therefore$  Since the depression (or elevation) is proportional to the concentration  $w$  grams of solute dissolved in  $W$  grams of solvent depress

the freezing (or elevate the boiling) point by  $\frac{1000 Kw}{MW}$  degrees.

Then, if  $\delta$  = the observed depression (or elevation)

$$M = \frac{1000 Kw}{\delta W}$$

\* These constants are sometimes expressed in terms of 100 grams of solvent; their numerical value is then 10 times greater.

It can be shown thermodynamically that

$$K = \frac{2T^2}{1000 L}$$

where  $T$  is the freezing (or boiling) point of the solvent on the absolute scale and  $L$  is the latent heat either of fusion or vaporization of the solvent according as the freezing point, or boiling point, is concerned in the experiment.

If  $K$  be known, either from the results of direct experiment, or from calculation as above,  $M$  can be found by measuring the change in freezing (or boiling point) of a solution of known concentration.

### § 8 Practical Methods for Finding Molecular Weights

Several methods for the determination of the molecular weights of substances have been given in earlier chapters, while a group of methods dependent, as has just been explained, upon the osmotic properties of dilute solutions must now be described. This is therefore a convenient place to summarize and classify the methods available, describing in detail those which have not been dealt with already.

The different ways in which the molecular weight may be found differ in their applicability, and this serves as a convenient basis for classification, so that we may divide the available methods as follows:

Methods available for

- |  |   |  |
|--|---|--|
| (1) Permanent Gases  | { | Regnault's method with extension to evaluation of limiting densities.                                    |
| (2) Substances which vaporize at ordinary pressures, without decomposition |   | Dumas's and Victor Meyer's methods.  |
| (3) Substances which decompose if vaporized at ordinary pressure           |   | Hoffmann's method.   |
| (4) Non-volatile substances which are soluble                              | { | Osmotic pressure, lowering of vapour pressure, elevation of boiling point, depression of freezing point. |
| (5) Bases (of known acidity)   |   | Titration, thermal decomposition of chloroplatinates.  |
| (6) Acids (of known basicity)  |   | Titration, thermal decomposition of silver salts.  |

**Regnault's method** has been described on page 28, Chapter 3, along with the Volumeter and Buoyancy methods, and the extension of the principle of molecular and atomic weight determination with a high degree of accuracy is discussed on page 111, Chapter 7.

The methods originated by **Dumas**, **Victor Meyer** and **Hoffmann** are described on pages 78–81, Chapter 5.

### Osmotic Methods

The methods named under heading (4) of the above classification are all based either directly or indirectly upon the osmotic pressure of a solution, and the theoretical connection between them has been indicated.

The actual determination of the osmotic pressure of a solution is a matter of considerable practical difficulty, and so is rarely used for molecular weight determinations in practice. Almost the only case of its use is in the determination of the so-called molecular weights of colloids. Methods employed for finding the osmotic pressures of solutions of substances like cane sugar have been described in § 2 of the present chapter.

The measurement of the **relative lowering of the vapour pressure** of a solution is also beset with practical difficulties if attempted directly, and although it has been employed with a certain measure of success in the hands of **Dieterici** and **Frazer**, it has not found wide application. Apart from this work, in so far as vapour pressure methods have been used, an indirect method known as the **air-saturation method** has usually been employed.

The principle of the method depends upon the fact that if dry air be passed over or through a solution it will take up vapour to an extent proportional to the vapour pressure of the solution; and if this air stream be now passed over, or through, a sample of the pure solvent it will take up a further quantity of vapour, proportional in amount to the difference between the vapour pressure of the solvent and that of the solution. If the vessels containing the solution and the solvent be weighed before and after the experiment, the loss in weight in each case will be a measure of the amount of vapour taken up by the air stream, so that (with the notation of § 6 of this chapter) we have

$$\frac{p_s}{p - p_s} = \frac{\text{loss of weight of solution}}{\text{loss of weight of solvent}}$$

By far the most important and widely used of osmotic methods are those dependent upon the elevation of the boiling point or depression of the freezing point.

The first really practicable method for evaluating the **elevation of the boiling point** of a solution was due to **Beckmann** and consisted in measuring as accurately as possible the boiling point of the pure solvent and afterwards of the solution formed by adding a known weight of solute. Precautions were taken to avoid error, but in spite of these it is not easy to avoid errors which are inherent in the method, such as superheating, fluctuations due to radiation, etc. Other ways of carrying out the experiment have accordingly been adopted.

When the solution of non-volatile solute boils, the vapour of the solvent and solute are in equilibrium; this condition can be established by leading the vapour of the boiling solvent into the solution. When the solution is at its boiling point, the vapour will pass through the system without condensation, and if the solution is below this temperature some vapour will condense, and the latent heat of condensation will continue heating the solution until the boiling point is reached. There is virtually no danger of superheating the solution. This principle

has been employed successfully in measuring the boiling points of solutions for molecular weight determinations. The method only works well, however, if the solvent has a large latent heat of vaporization and it suffers from the defect that the concentration of the solution is altered during the experiment by the condensed vapour of the solvent, and must be evaluated after each reading of the temperature.

It is now usual to employ apparatus using the principle suggested by Cottrell in 1919. In this method the bulb of the thermometer is in the vapour above the surface of the boiling liquid and this boiling liquid (solvent or solution as the case may be) is made to pump itself over the bulb of the thermometer. The form of the apparatus is indicated in Fig. 14.5. The tube *A* contains the boiling liquid (which is now usually heated electrically; this avoids the errors caused by draughts when gas heating is used). The side tube *B* leads to a condenser and the sheath *C* prevents condensed solvent from coming into contact with the bulb of the Beckmann thermometer\* *E*. The "pump" *D* consists of an inverted funnel as shown, dividing into three arms (two only are shown in the diagram) round the thermometer bulb. When the liquid in *A* is boiled bubbles and liquid trapped by the funnel are forced up the "stem" of the funnel and poured over the bulb. A thin layer of liquid which readily gets into equilibrium with vapour at atmospheric pressure thus covers the bulb and so the thermometer indicates the true boiling point free from errors caused by superheating or hydrostatic pressure.

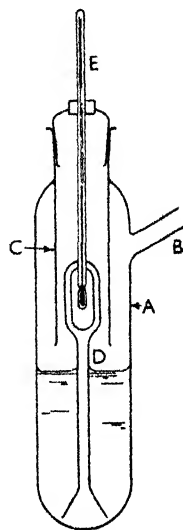


FIG. 14.5.  
Cottrell's  
Apparatus  
for Boiling-point  
Determinations

**Freezing-point depressions** are usually determined by means of Beckmann's apparatus, which is shown diagrammatically in Fig. 14.6. The tube *A*, Fig. 14.6, with a side neck *B*, is weighed, and about 15 ml. of the solvent are added, and the tube is weighed again. The Beckmann thermometer, reading to  $\frac{1}{100}$ th of a degree, and set so that the mercury is near the top of the scale when set for the freezing point of the solvent, has a reading lens *L*. The thermometer *T* and a stirrer *S* are placed in the solvent, and the whole arrangement is placed in a glass tube which serves as an air jacket. This is surrounded by a vessel of water or some liquid at a temperature about  $5^{\circ}$  below the freezing point of the solvent. This vessel is fitted with a stirrer *S*<sub>1</sub>. The temperature recorded by the thermometer

\* This thermometer has a reservoir of mercury at the top so that it can be set for use at any desired temperature as indicated in text-books of laboratory processes. A thermometer of this kind cannot be used to find actual temperatures, but it will give values for *small* differences in temperature. It can be adjusted so that these differences can be found in the neighbourhood of any desired temperature between  $-39^{\circ}\text{C}$ . and  $250^{\circ}\text{C}$

is allowed to fall until the solvent has supercooled; freezing is then started by vigorous stirring and the temperature rises to the freezing point proper. The thermometer should always be tapped before a reading is taken to make sure the mercury is not lagging behind. The highest point reached by the mercury in the thermometer is taken to be the freezing point of the solvent. Each determination should be repeated two or three times and the successive observations should agree within  $0.002^{\circ}$  to  $0.003^{\circ}$ . When the freezing point of the solvent has been determined, add a sufficient, weighed, amount of the substance under investigation to give a depression of  $0.3^{\circ}$  to  $0.5^{\circ}$ . After the freezing point has been determined again, find the freezing point after adding a second and then a third portion of the substance under investigation.

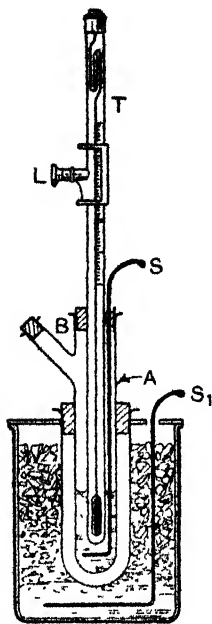


FIG. 14.6.—Beckmann's Apparatus for Freezing-point Determinations

The determination of the **molecular weights of acids** by either of the methods mentioned on page 207 depends upon a knowledge of the *basicity* of the acid concerned. The basicity of an acid (see page 342) may be defined as the number of hydrogen atoms in one molecule which are replaceable by a metal. If this number is known (see page 342 for methods of discovering it) we can find the molecular weight of the acid either by estimating the weight of it which will react with a gram-equivalent weight of a standard alkali by means of a titration of the kind common in volumetric analysis, or by finding the weight of metal in a known weight of one of its normal salts. The latter method is particularly useful in the case of *organic* acids which are usually weak acids and therefore not always satisfactory in a titration.

The metal usually employed in this process is silver. Since the silver salts are usually *normal* salts (cf. page 342), they are only sparingly soluble in most cases and hence readily prepared by precipitation, and are decomposed by heat, leaving a residue of metallic silver. The process consists then in the preparation of a pure dry sample of the silver salt, a weighed portion of which is ignited and the metallic silver residue is weighed. The equivalent weight of the acid is then: weight of salt containing 1 equivalent of silver —  $108 + 1$ , and hence

$$\text{Molecular weight of acid} = \text{equivalent weight} \times \text{basicity}.$$

The **molecular weights of bases** can be evaluated by processes analogous to the foregoing provided that the *acidity* (i.e., the number of equivalents of an acid which are neutralized by one molecular weight)



of the base is known. As with acids, the titration method is more applicable to inorganic bases; for organic bases use is made of the fact that they form, like ammonia (cf. page 945), crystalline chloroplatinates with platinic chloride of the general formula  $B_2H_2PtCl_6$  where  $B$  is a molecule of a mono-acid organic base. These chloroplatinates decompose on heating, leaving metallic platinum, the weight of metal contained in a known weight of chloroplatinate being thus determined. Then, the atomic weight of platinum is contained in one molecular weight of the salt, and therefore

Molecular weight of base

$$= \frac{\text{Molecular weight of salt} - \text{molecular weight of } H_2PtCl_6}{2}$$

### Examples

The following examples illustrate the methods of molecular weight determination discussed in this section.

Examples of the application of the limiting density method are given in Chapter 7 (page 111) and of vapour density methods in Chapter 5 (pages 78-81).

(1) *An aqueous solution of 1.0047 gm. of orthoboric acid per litre has an osmotic pressure of 28.8 cm. of mercury at 15°. What is the molecular weight of the acid?*

Since 1 gm.-molecule of a substance in 22.4 litres of solution will exert an osmotic pressure of 1 atm. at 0°, we have to discover what weight of boric acid dissolved in 22.4 litres at this temperature will have this osmotic pressure.

Since 1.0047 gm. in 1 litre has an osmotic pressure 288 mm. at 15°,

∴ 1.0047 gm. in 22.4 litres has an osmotic pressure  $\frac{288}{22.4}$  mm. at 15°,  
i.e., 1.0047 gm. in 22.4 litres has an osmotic pressure

$$\frac{288 \times 273}{22.4 \times 288} \text{ mm. at } 0^\circ$$

and  $\frac{1.0047 \times 22.4 \times 288 \times 760}{288 \times 273}$  gm. in 22.4 litres has an osmotic pressure 760 mm. at 0°.

$$= 62.63 \text{ gm.}$$

∴ 62.63 = molecular weight of boric acid.

(2) *When 108.24 gm. of mannitol were dissolved in 1000 gm. of water, the vapour pressure of the solution was found to be 17.354 mm. at 20°. At the same temperature the vapour pressure of water is 17.54 mm. What is the molecular weight of mannitol?*

It was shown on page 205 that  $\frac{p - p_s}{p} = \frac{PM}{RTs}$ . From this Raoult's Law can be deduced, viz.:

$$\frac{p - p_s}{p} = \frac{n}{N + n}$$

where  $n$  = number of molecules of solute.

$N$  = number of molecules of solvent.

For very dilute solutions this may be written:

$$\frac{p - p_s}{p} = \frac{n}{N}$$

Then if  $w$  = weight of solute

$W$  = weight of solvent

$m$  = molecular weight of solute

$M$  = molecular weight of solvent

we have:

$$\frac{p - p_s}{p} = \frac{\frac{w}{m}}{\frac{W}{M}}$$

$$\text{whence } m = \frac{wMp}{W(p - p_s)}$$

Substituting in this expression the values given, we have:

$$\begin{aligned} m &= \frac{108.24 \times 18 \times 17.54}{1000 \times 0.186} \\ &= 183.7 \\ &= \text{molecular weight of mannitol.} \end{aligned}$$

(3) *The boiling point of a solution of 0.1050 gm. of a substance in 15.84 gm. of ether was found to be 0.100° higher than that of pure ether. What is the molecular weight of the substance? (Molecular elevation for ether per 1000 gm. = 2.16°.)*

An elevation of 0.100° was produced by dissolving in 15.84 gm. of ether, 0.1050 gm. of substance.

∴ an elevation of 2.16° would be produced by dissolving in 15.84 gm.

of ether  $\frac{0.1050 \times 2.16}{0.100}$  gm. of substance

i.e., an elevation of 2.16° would be produced by dissolving in 1000 gm.

of ether,  $\frac{0.1050 \times 2.16 \times 1000}{0.100 \times 15.84}$  gm. of substance.

= 143.2 = molecular weight of substance.

(4) *The solution of 0.622 gm. of a substance in 40 gm. of water froze at -0.51°. What is the molecular weight of the substance? (Freezing point constant for water = 1.858 for 1000 gm.)*

A depression of  $0.51^\circ$  was produced by dissolving in 40 gm. of water, 0.622 gm. of substance.

$\therefore$  A depression of  $1.858^\circ$  would be produced by dissolving in 40 gm. of

$$\text{water } \frac{0.622 \times 1.858}{0.51} \text{ gm. of substance}$$

i.e., a depression of 1.858 would be produced by dissolving in 1000 gm.

$$\begin{aligned} \text{of water } & \frac{0.622 \times 1.858 \times 1000}{0.51 \times 40} \text{ gm. of substance} \\ & = 56.7 = \text{molecular weight of substance.} \end{aligned}$$

(5) On heating 0.3652 gm. of the silver salt of an organic acid until no further loss of weight occurred, there remained 0.172 gm. of silver. If the basicity of the acid is 1, what is its molecular weight?

0.172 gm. of silver is contained in 0.3652 gm. of salt

$$\begin{aligned} \therefore 108 \text{ gm. of silver are contained in } & \frac{0.3652 \times 108}{0.172} \text{ gm. of salt} \\ & = 229.3 \text{ gm.} \\ & = \text{molecular weight of the salt since} \\ & \quad \text{the acid is monobasic.} \end{aligned}$$

Therefore, if  $M$  = molecular weight of the acid, we have  $M = 229.3 - 108 + 1 = 122.3$ , for  $M$  will be the molecular weight of the salt less the atomic weight of silver, plus that of hydrogen.

(6) 0.7010 gm. of the chloroplatinate of a monoacid organic base gave 0.2303 gm. of platinum on heating. Calculate the molecular weight of the base.

Since 0.2303 gm. of platinum is contained in 0.7010 gm. of chloroplatinate,

$$\begin{aligned} 195 \text{ gm. of platinum are contained in } & \frac{0.7010 \times 195}{0.2303} \text{ gm. of chloro-} \\ \text{platinate} & \\ & = 594.2 \text{ gm.} \end{aligned}$$

This is the molecular weight of the salt  $B_2H_2PtCl_6$

$\therefore$  The molecular weight of  $B$

$$\begin{aligned} & = \frac{594.2 - 410}{2} \\ & = 92.1 \end{aligned}$$

410 being the molecular weight of  $H_2PtCl_6$ .

### § 9 Abnormal Molecular Weights

It will be evident from an inspection of the list of methods for measuring molecular weights given on page 207 that in many cases two or more methods can be employed for the same substance. Thus, for example, the molecular weight of iodine can be found either by one of the vapour density methods, or by the raising of the boiling point or depression of the freezing point of its solution in a suitable solvent, e.g., ether.

In many instances the results obtained by different methods show a satisfactory agreement; but there are a number of cases where the value for the molecular weight comes out either very much higher or very much lower than would have been expected. Such molecular weights are called **abnormal molecular weights**.

Thus, for example, the vapour density of acetic acid at 250° indicates a molecular weight of 60, which is in agreement with the formula which has been assigned to it on chemical grounds. But investigation of the effect of acetic acid on the freezing point of benzene leads to a value for the molecular weight very near to 120. That is to say, the observed depression of the freezing point, and hence the osmotic pressure of the solution, is only about half of what would be expected. Therefore the number of molecules present in the solution must be approximately half of what was supposed.

This result is explained on the assumption that acetic acid and substances exhibiting a like behaviour undergo **association**; that is to say, two or more molecules have combined to form a larger molecule. On this assumption, the depression of the freezing point (or other similar phenomenon) can be used in order to calculate the *degree of association*.

Abnormally great osmotic pressures (and hence elevations of the boiling point or depressions of the freezing point) are observed principally in the case of solutions of acids, alkalis and salts. All acids and alkalis, except very weak ones (cf. page 219), and practically all salts, are found to have an abnormally high osmotic pressure in solution in water, whereas in most other solvents the value is about what is to be expected from the chemical evidence, vapour density data and so forth. For example, hydrochloric acid gas has a density as determined from absolute density measurements, or from effusion experiments, corresponding to a molecular weight of about 36.5; whereas as calculated from the freezing point of its solutions in water its molecular weight is close to 19. Clearly something akin to the converse of association is taking place—the development of this theme, however, belongs to the next chapter.

## CHAPTER 15

# ELECTROLYSIS AND THE ELECTROLYTIC DISSOCIATION THEORY

The electricity which decomposes, and that which is evolved by the decomposition of a certain quantity of matter, are the same.—M. FARADAY.

In framing hypotheses we must see that they agree with facts; in other respects they may be as inconceivable (not self-contradictory) as any fairy tale.—M. M. P. MUIR.

### § 1 The Conduction of Electricity in Liquids

THE fact that a current of electricity will pass through materials such as copper wire has become a commonplace of everyday life; and further, it is well known that, whereas some substances such as copper (or, in fact, metals generally) will allow such a current to flow, others, as for example glass or rubber, will not do so. The former are called **conductors**; the latter **insulators** or **non-conductors**.

In a similar way, when we come to investigate the behaviour of solutions, we find that some will conduct a current, while some will not do so. Substances whose solutions are conductors are called **electrolytes**; those whose solutions are non-conductors are termed **non-electrolytes**.

Investigation of the phenomena associated with the passage of electricity through solutions of electrolytes shows that they differ markedly from the corresponding behaviour of metallic conductors. Thus metallic conductors do not appear to undergo any chemical change due to the passage of a current, whereas a solution of an electrolyte shows evidence of chemical action, for gases are often liberated and other chemical changes can be observed.

For example, if a source of electricity such as an accumulator be connected to two platinum plates which are immersed in a solution of copper sulphate, we see, as soon as the circuit is complete, that bubbles of gas appear on one of the platinum plates, viz., that which is connected to the positive pole of the accumulator. The other plate begins to turn pink, owing to the deposition of a thin film upon it. Investigation shows that the gas is oxygen and the pink film is copper. If the current is allowed to pass for a sufficient length of time, the blue colour of the solution will fade gradually and a solution of sulphuric acid will be left. If the plate from which the oxygen is being liberated be immersed, at the beginning of the experiment, in copper sulphate solution contained in a porous pot, the pot itself being immersed in copper sulphate solution into which the other plate also dips, we shall

find that the sulphuric acid is formed round this plate. Clearly, considerable chemical changes are taking place, but the process differs from ordinary cases of chemical change in that a current of electricity is necessary in order to bring them about, and the products of the change make their appearance at points which may be separated by a considerable distance. This process of the passage of a current through a solution of an electrolyte with its resulting chemical change is called **electrolysis**, and the plates or other conductors dipping into the solution by means of which the current enters and leaves it are known as **electrodes**. The electrode by which the current *enters* the solution is termed the **anode**: that by which it leaves, the **cathode**. The anode is thus the *positive* electrode, and the cathode the *negative* electrode.

Phenomena akin to those just described occur only with liquids; these liquids being either solutions of acids, alkalis, and salts, or fused compounds, such as alkalis and salts.

It is noticeable that such compounds all consist of two portions, an acidic radical and a basic radical (see page 340), and the process of electrolysis appears to separate these two halves and cause them to appear at the electrodes. The acidic radical appears to be liberated at the anode, and the basic radical at the cathode. These two parts of the substance were termed **ions** by Faraday, those which appear at the anode being called **anions**, and those which are liberated at the cathode, **cations**.

## § 2 Faraday's Laws of Electrolysis

It has been known for a very considerable period that an electric current will decompose an electrolyte; and application was made of this fact by Davy early in the nineteenth century, for it was by this means, for example, that he first isolated sodium.

The first thorough quantitative study of electrolysis was made by Faraday in 1834 and he thereby discovered two laws of fundamental importance which are known as **Faraday's Laws of Electrolysis**. These are:

- (1) the mass of substance decomposed is directly proportional to the quantity of electricity passing through the solution;
- (2) when the same current is passed for the same time through several electrolytes in series, the masses of each substance liberated are proportional to their chemical equivalents.

Faraday measured carefully the amount of substance liberated by one coulomb (i.e., the unit quantity of electricity) and hence the quantity of electricity required to liberate the chemical equivalent of any substance is known. One coulomb will deposit 0.001118 gm. of silver; and hence 107.88 gm. of silver (i.e., the equivalent of silver) will be deposited by 96,494 coulombs of electricity. Thus it follows that Faraday's Laws can be summed up in the statement that **one**

gram-equivalent of any substance is liberated by the passage of 96,494 coulombs of electricity. This quantity of electricity is known as a Faraday (not to be confused with the farad, the unit of *capacity*).

### § 3 The Mechanism of Electrolysis

The first attempt to explain the phenomena of electrolysis was that of Grotthus who, in 1805, put forward his chain theory. He supposed that the passage of the current through the solution and the chemical decomposition accompanying it are brought about by the successive decomposition and recombination of the particles of the dissolved substance. This is illustrated in Fig. 15.1, where  $A B$  represents a molecule of the electrolyte;  $A$  and  $B$  being oppositely charged "halves" of it where  $A$  is the cation and  $B$  is the anion. According to this theory, as soon as the electrodes are connected up to a source of electricity the molecules are turned so as to arrange themselves as shown in line I (Fig. 15.1). Owing to the polarity of the electrodes,  $A$  and  $B$  are

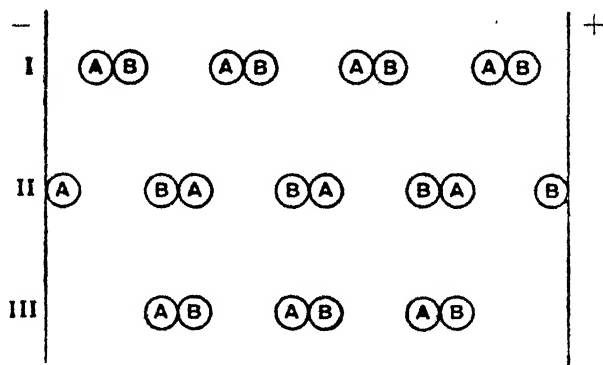


FIG. 15.1.—Grotthus's Theory

supposed to be attracted. Consider the attraction of  $A$  to its electrode. This splits it off from the part  $B$  to which it was attached, and the part  $B$ , finding itself free, attacks the molecule next to it, depriving it of its  $A$  portion. This process goes on along the line, a part  $B$  being similarly attracted to the other electrode. This is illustrated in line II (Fig. 15.1). The parts  $A$  and  $B$  attracted to the electrodes are liberated and the state represented by line II (Fig. 12.1) results, the position being the same as at the beginning except that the molecules are all the opposite way round. The attraction of the electrodes will, therefore, cause them to turn over and the sequence of changes described will be repeated (line III).

This theory of Grotthus had to be given up as soon as it had been shown that Ohm's Law applies to electrolytes. This means that all the energy of the current is utilized in overcoming the resistance of the

solution and none in the splitting of the molecules, as would be required by Grotthus's theory.

After the Grotthus theory had been disproved, the next real attempt to explain electrolysis was due to **Clausius** who, in 1857, suggested that in solution an electrolyte is split up into ions whether a potential difference was applied to it or no, and that at all times there is in the solution an equilibrium between these ions and the whole molecules of the electrolyte. These ions were supposed to be charged and, therefore, would travel towards one or other electrode when these are placed in the solution, there to be discharged and liberated as the ordinary products of electrolysis. Clausius, however, supposed that only a very minute proportion of the electrolyte was split up into ions.

This theory of Clausius was satisfactory up to a point; but it made no real attempt at a quantitative explanation. The extension of Clausius's theory in this way was made by Arrhenius.

The Theory of Electrolytic Dissociation, or the Ionic Theory as it is often called, as put forward by **Arrhenius** in 1887, supposes that all electrolytes are dissociated in greater or less degree in solution, the products of this dissociation being ions. These ions consist of atoms, or groups of atoms (the acidic or basic radicals of the dissolved substance), carrying charges numerically equal to the valency of the radical in question. The total charge on the ions at any time will thus be algebraically equal to zero. The formation of these ions is considered to be a partial and reversible process which is most nearly complete in very dilute solutions.

The facts of electrolysis are readily accounted for by this theory, and Faraday's Laws also. For the presence of the ions in the solution, quite apart from the insertion of electrodes, accounts for the fact that the solution obeys Ohm's Law, on the assumption that the current is carried by the movement of the ions to the electrodes. The appearance of the products of electrolysis at widely separate points (i.e., at the electrodes) is also explained.

If we assume that any univalent ion carries a charge of magnitude  $e$ , since the current passes by the discharge of ions, the quantity of electricity which passes through the solution will depend upon the number of ions discharged. As each ion of the same valency carries the same charge, the current will be proportional to the number of ions discharged, and hence to the mass of substance liberated. This is Faraday's First Law of Electrolysis.

A quantity of electricity  $e$  will be carried through the solution by one ion carrying this charge and will involve the liberation of that one ion. If the ion carries a charge  $2e$  (i.e., if it be a bivalent ion) twice the quantity of electricity will be involved in the discharge of the ion. Hence we see that, since the charge of an ion is equal to  $e$  multiplied by the valency of the ion, the quantity of substance liberated by the passage of a current corresponding to  $e$  units will be equal to the weight



of the ion divided by its valency; that is, to one equivalent of the ion. This is Faraday's Second Law in another form.

The further quantitative verification of the Ionic Theory by Arrhenius depended upon two distinct phenomena, viz.: (1) the abnormal molecular weights of electrolytes as revealed by the osmotic properties of their solutions, and (2) measurements of the conductivity of solutions at different dilutions.

#### § 4 The Ionic Theory and Osmotic Phenomena

Mention has been made in the preceding chapter (page 214) of the fact that solutions of acids, alkalis and salts show an abnormally high osmotic pressure, and hence give abnormally low values for the molecular weights of the dissolved substances. It is found that these abnormal values are a specific property of electrolytes, and Van't Hoff in developing his theory of solution introduced a factor  $i$  (known as the Van't Hoff Factor) into the equation  $PV = RT$  when this was to be applied to solutions of electrolytes so that it then read (for one gram-molecule of solute)

$$PV = iRT.$$

The value of  $i$  as determined from freezing-point measurements is found to vary with the dilution of the solution, and also with the nature of the solute, in a regular way. Thus, for sodium chloride and similar uni-univalent salts it has a value 1.8 approximately in moderately strong solutions, but increases with dilution to a value close to 2.0 at high dilution. Sodium sulphate gives a value for  $i$  which similarly varies from 2.2 to approximately 3.0.

This behaviour resembles that of certain gases whose vapour density is anomalously low in comparison with the value which would be expected from other evidence. Ammonium chloride vapour is a case in point (see page 214). This result has been shown to be caused by the dissociation of the ammonium chloride when in the vapour state into ammonia and hydrogen chloride. As the osmotic phenomena of solutions are seen to be, in general, analogous to the behaviour of gases, and in particular are colligative properties, Arrhenius suggested that the Van't Hoff factor  $i$  was the result of the dissociation of molecules of electrolyte into ions giving more particles than in an ordinary solution. Thus, if 1 gram-molecule of an electrolyte which dissociates into  $n$  ions be dissolved in 1 litre of water, and if the fraction  $\alpha$  of the molecules be dissociated, there will be in the solution  $1 - \alpha$  gram-molecules of undissociated electrolyte and  $n\alpha$  gram-molecules of ions. There will thus be  $(1 - \alpha) + n\alpha = 1 + (n - 1)\alpha$  gram-molecules of solute altogether. The depression of the freezing point of the solution will therefore be greater than if no dissociation had occurred in the ratio

$$1 + (n - 1)\alpha : 1$$

But this ratio is  $i$ ,

$$\therefore i = 1 + (n - 1)\alpha$$

$$\text{or } \alpha = \frac{i - 1}{n - 1}$$

Applying the reasoning to a sodium chloride solution, for which  $i = 1.85$ , this would suggest that the salt is 85 per cent dissociated at this particular dilution.

Arrhenius confirmed this view by a comparison of the values obtained for  $i$  in various solutions with those for the electrical conductivity of similar solutions. For, according to him, the conductivity of a solution is determined by the number of ions present, and so should show a close correspondence with the value of the factor  $i$ .

TABLE XVIII.—DEGREE OF DISSOCIATION FROM FREEZING POINT AND CONDUCTIVITY MEASUREMENTS

Substance	Volume in litres, containing 1 gm.-mol.	$i$	$\alpha$ -from freezing point	$\alpha$ -from conductivity
Potassium chloride .	200	1.96	0.96	0.97
	20	1.88	0.88	0.90
Potassium nitrate . .	200	1.96	0.96	0.95
	20	1.85	0.85	0.87
Hydrochloric acid . .	200	1.99	0.99	0.98
	10	1.91	0.91	0.92
Nitric acid . .	200	1.97	0.97	0.98
	5	1.87	0.87	0.92
Sodium hydroxide .	200	1.99	0.99	0.96
	20	1.83	0.83	0.91
Calcium nitrate . .	20	2.41	0.70	0.73
	10	2.41	0.70	0.68
Potassium ferrocyanide .	40	3.32	0.58	0.54
	10	2.79	0.45	0.46

### § 5 Measurement of the Conductivity of Solutions

The problem of a suitable experimental technique for finding the conductivity of solutions was solved by Kohlrausch in 1869 and following years, and most of the important work in this field has been based on his methods.

When a metallic conductor is included in an electrical circuit, it offers a certain resistance to the passage of the current, which resistance depends upon the length and cross-section of the conductor as well as upon the material of which it is made. The latter factor is

defined by the *specific resistance* of the material, which is the resistance (usually measured in ohms\*) of a cube of the substance whose edges are 1 cm. long. The reciprocal of this quantity is called the **specific conductivity** and is measured in *reciprocal ohms* or **mhos**. Calculations involving metallic conductors usually employ the *resistance* of the conductor; for solutions it has proved more convenient to employ the *conductivity*.

Another distinction between solutions and metallic conductors is that the conductivity of the former does not depend upon the whole of the material between the electrodes but only upon the ions present. Hence, the comparison of the conductivity of two solutions should be made with solutions containing equivalent amounts of solute, and the quantity most commonly employed in the investigation of solutions is the **equivalent conductivity**, which may be defined as the **conductivity of a solution containing 1 gram-equivalent of the solute when placed between two electrodes of indefinite size 1 cm. apart**. This quantity, the equivalent conductivity, is usually represented by the symbol  $\lambda$  and is equal to the specific conductivity multiplied by the volume of solution which contains 1 gram-equivalent.

The term **molecular conductivity** is sometimes employed and represents similarly the conductivity of a solution containing 1 gram-molecule of the solute, under the above conditions.

The determination of the equivalent conductivity of a solution thus depends, primarily, upon finding the resistance of a portion of solution of known strength, between electrodes of known area and fixed distance apart. It is here that the principal difficulties arise, for if the measurement be carried out in the same way as for a metallic conductor, using a direct current, electrolysis occurs with the liberation of gases which cause the setting up in the solution of a back electromotive force (or polarization E.M.F.) which completely masks the resistance of the solution alone. This difficulty was surmounted by Kohlrausch who used an alternating current from an induction coil, in conjunction with the ordinary Wheatstone Bridge arrangement for the measurement of resistance, the arrangement employed being shown diagrammatically in Fig. 15.2.

The terminals of a source of alternating current  $I$  are connected as shown;  $ab$  is the bridge wire (which is usually one metre long and lies along a metre-scale.  $R$  is a resistance-box and  $V$  is a conductivity vessel containing the solution under examination. On account of the use of alternating current, the null point on the wire  $ab$  cannot be found by using a galvanometer as detecting instrument as in the ordinary Wheatstone Bridge arrangement; a telephone is therefore

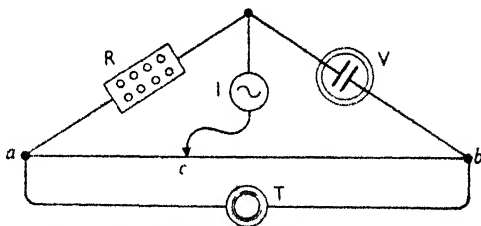


FIG 15.2—Measurement of Conductivity of Electrolytes

\* The international standard ohm is the resistance at 0° C. of a column of mercury 106.3 cm. long and weighing 14.4521 gm. (i.e., of 1 sq. mm. cross-section).

used as detecting instrument, the slide *c* being moved until there is a minimum of sound in the telephone. When this point has been found:

$$\frac{R}{V} = \frac{ac}{cb} \text{ or } V = R \cdot \frac{cb}{ac}$$

where *V* = resistance of the solution  
and *R* = resistance in the resistance-box.

Various forms of cell are employed in work of this kind. A type frequently used consists of a small cylindrical glass vessel with parallel platinized platinum electrodes. These are rigidly sealed into glass tubes and connection is made to them by means of mercury (Fig. 15.3). The electrodes are electrolytically coated before use with a layer of platinum black, the sharpness of the minimum in the telephone being thereby much improved. The glass tubes are fixed in position by means of an ebonite or plastic lid, and during a determination the whole cell is immersed in a thermostat, since the conductivity of a solution is markedly affected by changes of temperature.

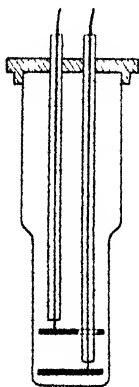


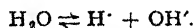
Fig. 15.3.  
Conductivity  
Cell

For approximate work an induction coil will serve as the source of alternating current, but it is liable to be noisy, and as it does not give a really symmetrical current it does not eliminate polarization entirely. For accurate work therefore a thermionic valve oscillator is now almost always used as the source of A.C.

The specific conductivity of a solution is, as we have seen, the conductivity of a centimetre cube of the solution. But, in general, the electrodes of a conductivity cell will not be exactly 1 sq. cm. in area, nor exactly 1 cm. apart, so that the value determined by experiment for the conductivity will have to be multiplied by a factor to give the specific conductivity. Since this factor evidently depends only upon the dimensions of the cell it is usually determined by finding the conductivity in the cell of a solution of known conductivity, whence this factor, known as the **cell constant**, can be calculated and used in subsequent measurements. For this purpose use is generally made of Kohlrausch's values for the conductivity of potassium chloride solutions.

### Conductivity Water

In exact measurements of conductivity, and particularly at high dilutions, it is necessary that the water used for making the solutions should be as pure as possible. It has been found that ordinary distilled water still has a considerable conductivity (caused by the presence of traces of dissolved electrolytes and of gases such as carbon dioxide), and for conductivity work of a high order of accuracy a much purer water, known as **conductivity water**, is required. The purest possible water still has a very slight conductivity owing to the fact that water is itself very slightly ionized:



The conductivity of this ultra-pure water is about  $0.043 \times 10^{-6}$  mho at 18° C., while that of ordinary distilled water is usually in the neighbourhood of 3 to 6  $\times 10^{-6}$  mho at 18° C.

For most conductivity work, a water having a conductivity of about  $0.9 \times 10^{-6}$  mho is employed. This is known as **equilibrium water** and is obtained by careful redistillation of ordinary distilled water over acidified potassium permanganate, then from a little barium hydroxide, and then finally into a block tin condenser in a stream of carbon dioxide-free air. For work of a very high order of accuracy, or when solutions of very low conductivity are being investigated, conductivity water proper is required. In the preparation as described above, if only a part

of the water is condensed, and the remainder allowed to escape as steam and carry off with it the gaseous impurities, water of conductivity as low as  $0.1 \times 10^{-6}$  mho can be obtained. This water can only be used when air is rigidly excluded.

An alternative, and simpler method for obtaining conductivity water, which is now available, makes use of ion-exchange resins (cf. page 311). A mixture of anion- and cation-exchange resins is used and when a stream of water is passed slowly through it the anions present are replaced by hydroxyl ions and the cations by hydrogen ions and thus the water is "de-ionized" completely. The resins can be regenerated by first separating them and then treating the anion exchanger with excess of sodium hydroxide solution and the cation-exchange resin with excess of hydrochloric acid.

### § 6 Equivalent Conductivity and Concentration—Kohlrausch's Law

Kohlrausch found, on examining the values he had obtained for the equivalent conductivities of solutions of different concentration, that the equivalent conductivity of all electrolytic solutions increases with dilution; and further, that with increasing dilution the equivalent conductivity tends towards a maximum, usually referred to as the equivalent conductivity at infinite dilution.

Another generalization put forward by Kohlrausch is that *the equivalent conductivity at infinite dilution is the sum of two values, one depending on the cation and one on the anion*. That is,  $\lambda_{\infty} = l_c + l_a$  where  $\lambda_{\infty}$  is the equivalent conductivity at infinite dilution, and  $l_a$  and  $l_c$  are called the **mobilities** of the ions. This is known as **Kohlrausch's Law**, and has an important application in the quantitative development of the Ionic Theory by Arrhenius.

According to the electrolytic dissociation theory of Arrhenius, the equivalent conductivity of a solution depends upon the number of ions present and the increase in equivalent conductivity with dilution is interpreted to mean that the proportion of the solute molecules which have become dissociated into ions is increasing, the limit being reached when complete dissociation has occurred. That being so, the **degree of ionization**—represented by  $\alpha$ —at any given dilution will be given by the ratio of the equivalent conductivity of a solution of that degree of dilution ( $\lambda_c$ ) to the equivalent conductivity of the same solute at infinite dilution ( $\lambda_{\infty}$ ) or

$$\alpha = \frac{\lambda_c}{\lambda_{\infty}}$$

This ratio is often expressed in practice as a percentage.

The value of the equivalent conductivity at infinite dilution can be obtained easily by extrapolation in the case of substances which show high equivalent conductivity at moderate dilutions (the so-called strong electrolytes); in the case of so-called weak electrolytes Kohlrausch's Law is made use of, the component of the total conductivity due to each ion being determined from the equivalent conductivities of strong electrolytes derived from these ions. Thus, the conductivity of acetic acid at infinite dilution is calculated from the experimentally

determined values for sodium acetate, hydrochloric acid and sodium chloride, which are all strong electrolytes:

$$\lambda_{\infty} \text{ (for sodium acetate)} = 78.5 = l_{\text{Na}^+} + l_{\text{Ac}^-} \quad (1)$$

$$\lambda_{\infty} \text{ (for hydrochloric acid)} = 380.4 = l_{\text{H}^+} + l_{\text{Cl}^-} \quad (2)$$

$$\text{and } \lambda_{\infty} \text{ (for sodium chloride)} = 109.0 = l_{\text{Na}^+} + l_{\text{Cl}^-} \quad (3)$$

$$\therefore \lambda_{\infty} \text{ (for acetic acid)} = l_{\text{H}^+} + l_{\text{Ac}^-} = (1) + (2) - (3) = 349.9.$$

The results obtained by Arrhenius for the degree of ionization of various electrolytes at different degrees of dilution from calculations thus based on conductivity measurements agreed extremely well with the values deduced from the Van't Hoff factor in the investigation of the osmotic properties of solutions (see § 4 above).

### § 7 Statement of the Electrolytic Dissociation Theory

According to Arrhenius, when an electrolyte is dissolved in water its molecules undergo, to a greater or less degree, dissociation into positive and negative ions. These ions behave as independent entities, having their own specific properties and reactions. To them are due the electrical properties of the solution, the abnormal osmotic properties, and the characteristic behaviour of all the salts of a given metal or a given acid.

#### Evidence in Support of the Ionic Theory

(1) It provides a satisfactory explanation of the phenomena of electrolysis, both quantitatively and qualitatively (see § 3); and also enables the behaviour of voltaic cells in the production of electricity to be explained (§ 10).

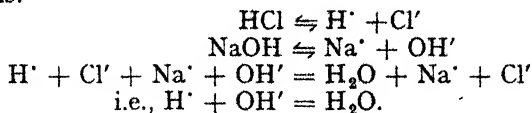
(2) It explains the increase in equivalent conductivity of solutions with increasing dilution, and also the difference in the equivalent conductivity of solutions of different electrolytes (§ 6).

(3) Solutions of electrolytes show additive properties. Thus, for instance, all copper salts give blue solutions (the same blue); the colour of permanganate solutions is similarly independent of the nature of the cation; all sulphates which are soluble in water give characteristic reactions. These facts are readily explained by the existence in the solution of the respective ions, free and uncombined.

(4) The "abnormal" osmotic phenomena exhibited by electrolytes (high osmotic pressure, large depression of the freezing point) can be accounted for, and are in quantitative agreement with, the results of conductivity measurements.

(5) The equivalent heat of neutralization (i.e., the heat evolved when 1 gram-equivalent of an acid reacts with 1 gram-equivalent of an alkali) is the same for all strong acids and bases. This follows from the ionic theory, according to which (since the salt produced is itself an electrolyte) the process consists in the formation of water (which is

only very slightly ionized since when pure it has a very low conductivity). Thus:



(6) Reactions between electrolytes are very rapid, while those of non-electrolytes are usually slow.

(7) Evidence in favour of the existence of ions has also been furnished by modern work on the structure of the atom and the nature of valency (see page 155); and also by the results of the investigation of the structure of crystals (page 198).

### Evidence against the Ionic Theory

Many objections have been levelled against the Ionic Theory; a natural enough circumstance in view of its startling nature, when first suggested. The following are some of the principal criticisms which have been urged against it:

(1) The ions produced would be, in many cases, substances which would react with water, e.g., sodium.

(2) The affinity between the different parts of the molecule (e.g., sodium and chlorine in sodium chloride) is very great; how can mere solution in water serve to separate them?

(3) If free ions are present in the solution as definite entities, it ought to be possible to separate them by diffusion or some other mechanical process.

(4) Compounds like mercurous chloride, very prone to thermal dissociation (see Chapter 31, page 727), are not readily ionized; while compounds like calcium chloride, which resist thermal dissociation, are readily ionized. Would not the Ionic Theory predict the opposite?

(5) Why do not the ions which carry large charges recombine, being then held by the normal attraction between oppositely charged bodies?

These objections have been met to a large extent, the more so since some of them rest upon a confusion between the nature of an ion and an uncharged atom.

Thus it was held from the start that a charged atom of sodium (i.e., a sodium ion) is very different from an uncharged sodium atom, and hence it does not react with water. The same answer was made to the objection that the affinity, for example, between the sodium and chlorine in sodium chloride was so great that mere solution would not separate them; since the separation required by the theory is into *ions* and not into the original atoms.

This explanation is now felt to have even greater weight than was

understood when it was first put forward, for according to modern views (Chapter 11, page 155) the sodium atom very readily parts with an electron to form a sodium ion which has the same electronic configuration as the very stable neon atom. Similarly, the chlorine atom very easily takes up an electron to reproduce the stable electronic configuration of an argon atom. Furthermore, it has also been shown, as was suggested by Ostwald, that a large amount of energy is evolved in this process; that is, in the formation of an ion from an uncharged atom.

We now know also that even in the crystal, substances like common salt exist in the form of ions, being held together by purely electrostatic forces. The influence of these forces is weakened when exerted in a medium of high dielectric constant, for the work done in separating two opposite electrical charges is inversely proportional to this constant. Hence, the degree of ionization of a given substance should vary with the dielectric constant of the solvent, and to a large extent this has been shown by experiment to be the case. This answers objections (2) and (5) as water has a very high dielectric constant. This effect is, however, masked in some instances by the property of the ions of combining with the solvent to an extent sufficient to give it the preponderating influence, thus accounting for the variations which have been observed from strict proportionality between dielectric constant and degree of ionization.

The criticism that separation ought to be practicable has been met by pointing out that the electrical charges would tend to cause the ions to arrange themselves in the solution in a quasi-pattern which would make separation difficult, though not impossible. In fact, such a separation is believed to have been effected by Tolman (1911) by centrifuging solutions of sodium, potassium and hydrogen iodides, when the ends of the tubes acquired charges of an opposite kind, presumably through the heavy iodide ions having been accumulated at one end. This evidence has been questioned by some, who have attributed the production of the charges to the same cause as other electrical effects which can be produced by rapid motion in the air.

The lack of direct proportionality between thermal and electrolytic dissociation must also be ascribed to the difference in the nature of these processes. Thermal dissociation produces uncharged atoms or molecules, presumably on account of the increase in molecular agitation at higher temperatures as postulated by the Kinetic Theory. But the separation of ions is brought about, as already mentioned (page 155, Chapter 11, and above), by the placing of the substance in a medium of high dielectric constant, thus weakening the magnitude of the purely electrostatic forces which previously held the ions together.

In consequence of the objections mentioned, and others of a like nature, attempts have been made, from time to time, to work out other theories to explain the observed phenomena of electrolysis, and the behaviour of solutions of electrolytes in general. These have usually been based upon the assumption



of the formation of complexes by reactions between molecules of the solvent of different degrees of complexity, and hence of differing constitution, with the molecules of the solute. Notable among these theories is that of H. E. Armstrong, but so far the Electrolytic Dissociation Theory holds the field since, in spite of difficulties, it affords the most consistent explanation of the fundamental facts which has so far been put forward.

### § 8 Modern Developments and the Ionic Theory

In certain directions the theory as put forward by Arrhenius has undergone modification in recent years; principally at the hands of Debye, Hückel, and Onsager. These modifications have been suggested in the attempt to meet two difficulties, viz., first the fact that modern knowledge of the structure of the atom and the nature of crystals (Chapter 10; Chapter 13, page 198) has shown that a crystal of an electrolyte consists already of ions held together only by electrostatic forces; and secondly, the apparent failure of the Law of Mass Action (Chapter 18, page 262) to account for the behaviour of strong electrolytes.

The former of these points to the view which is now put forward by Debye and Hückel of a **theory of complete ionization**, according to which it is concluded that solution of a salt in water involves merely the separation of the groups of pre-existent ions. The latter difficulty is also to some extent explicable by this hypothesis. The Law of Mass Action which, as will appear (Chapter 17), affords a quantitative explanation of many diverse chemical equilibria, when applied to electrolytes satisfactorily agrees with the results of experiment only for weak electrolytes; that is, electrolytes whose equivalent conductivity is but small at considerable dilutions. For strong electrolytes there is no semblance of agreement between experiment and theory based upon the Arrhenius view of Electrolytic Dissociation.

The Debye-Hückel Theory attempts to meet both these difficulties by postulating, in the case of strong electrolytes, complete ionization at all dilutions. Increase in the value of the Van't Hoff factor  $i$ , i.e., in the osmotic activity of the solution, or of the equivalent conductivity, is ascribed not to increase in the number of the ions, but to an increase in what is termed the **ionic activity**. The mass law is based on the assumption that the various kinds of molecules concerned in a reaction are subject to no attractive or repulsive forces and that molecular collisions are due to chance. This assumption cannot be valid when the "molecules" in solution are charged particles. Hence, when the Law of Mass Action is applied to ions, the observed concentration,  $c$ , of a given ion must be corrected to allow for the electrical and other effects of the ions on one another. The correction factor,  $f$ , is termed the *activity coefficient*, and the corrected concentration, the *activity*,  $a$ , for a given ion, so that  $a = cf$ . The activity is thus an *effective* concentration, the true "active mass" of the mass law.

Debye and Hückel examined the effect of electrical restraints on the conductivity due to ions in a solution. They supposed, as already stated, that there is complete ionization for strong electrolytes and that the mobility of the ions is affected mainly by two kinds of electrical restraints.

The attractions between positive and negative ions will result in there being an excess of negative ions round each positive ion, and vice versa, providing what they term an *ionic atmosphere* round each ion. (The arrangement thus suggested would be similar to that obtaining in a sodium chloride crystal—page 198.) When an ion begins to move under the influence of an applied potential difference, this ionic atmosphere has to be built up in front of the moving ion, while that behind it dies away. It is supposed that the formation of the new atmosphere lags behind the decay of the old, the time interval being known as the *relaxation time*. There will thus always be an excess of ions of opposite sign to the moving ion behind it, which will cause its movement to be retarded. In addition, the applied potential difference will tend to move the ionic atmosphere itself in a direction opposite to that of the moving ion which will cause further retardation

of the latter. These effects will be larger the greater the concentration, and so with increasing dilution, the speed of a given ion, under a given potential gradient, will increase and with it the equivalent conductivity, reaching a maximum at infinite dilution.

As a result of their mathematical analysis of these effects, Debye and Hückel showed that the effect of the retardations mentioned should be proportional to the square root of the concentration, i.e.

$$\lambda = \lambda_{\infty} - a\sqrt{c}$$

where  $\lambda$  = conductivity at concentration  $c$  and  $a$  is a constant for a given solvent and temperature.

This theory has met with a certain measure of success when applied to dilute solutions, but its range of applicability is very limited and it is evident that the theory is far from complete. It is now recognized that there is an element of truth in the original electrolytic theory, and that as our knowledge grows, attempts to apply that theory to the facts will approach more and more closely to a more complete explanation of those facts.

### The Hydration of the Hydrogen Ion

Another modification of the details of the Electrolytic Theory, as put forward by Arrhenius, in consequence of the results of later work, is necessitated by the fact that ions are usually hydrated, i.e., they carry with them a certain amount of water. The existence of this hydration has been shown by measuring the change in concentration of a non-electrolyte, present in the solution, which occurs as a result of electrolysis. Evidence has accumulated to show that, for instance, in a solution of an acid it is not hydrogen ions themselves which are present, but positively charged ions of the formula  $[H_3O]^+$ , known as **hydroxonium ions**. One of the important consequences of this fact is referred to in Chapter 18 (page 269) in connection with the strength of acids.

### § 9 Voltaic Cells

It has long been known that if plates of two dissimilar metals are connected by a wire and immersed in a solution of an electrolyte, a current will flow along the wire. If plates of zinc and copper are taken and immersed in dilute sulphuric acid the arrangement is known as a **simple cell**. If the cell is allowed to work for a little time it will be found that zinc is dissolving in the acid and that bubbles of hydrogen appear on the copper plate, which is not otherwise affected. If the strength of the current passing through the wire be investigated, it will be found that by the time the copper plate has become covered with hydrogen the current has dropped almost to zero. On brushing away the bubbles from the copper plate the current will rise again to its former value.

In normal electrical terms, it is found that a current is flowing along the wire from the copper to the zinc; although, in fact, it is now known that a stream of electrons is passing along the wire from the zinc to the copper. Zinc is going into solution, forming a solution of zinc sulphate; or, in terms of the ionic theory, zinc ions  $Zn^{++}$ , that is,

atoms of zinc carrying double positive charges. The formation of a zinc ion, which has thus two electrons fewer than the atom from which it is derived, will thus leave the zinc plate with these two electrons, which are conducted through the wire to the copper plate. In the solution there are hydrogen ions, caused by the dissociation of the acid (see Chapter 18). When the copper plate receives the two electrons, by way of the connecting wire, it becomes negatively charged and hence attracts hydrogen ions (i.e., hydrogen atoms each having lost one electron) which are positively charged, and these take up electrons from the copper plate, so becoming hydrogen atoms again and being liberated as hydrogen gas. The production of the current is thus seen to depend upon the tendency of the zinc atoms to become zinc ions, concerning which more is said in the next section.

The simple cell is not a useful cell on account of the tendency for its activity to be stopped by the accumulation of hydrogen on the copper plate, a phenomenon which is known as **polarization**. In consequence, various other forms of cell have been devised in order to avoid this difficulty. The usual method for avoiding it is to replace the copper by carbon and to surround this with an oxidizing agent which oxidizes the hydrogen to water as soon as it is formed. Some cells, however, employ two liquids, as, for example, the Daniell cell, which consists of a plate of zinc immersed in dilute sulphuric acid contained in a porous pot, the whole standing in a solution of copper sulphate in which there is also a copper plate. In this the zinc dissolves as before, but the copper plate, when negatively charged, attracts not hydrogen ions but copper ions which, when discharged, are deposited on the copper plate as metallic copper. Thus no change in the working of the cell occurs.

The most important form of cell at the present time is the Leclanché cell, particularly in the form of the so-called dry cell, the manufacture of which for use in portable radio sets, hearing-aids, pocket torches and for similar purposes has become an important industry.

The ordinary Leclanché cell consists of a carbon rod in a porous pot surrounded by a mixture of powdered carbon and manganese dioxide. The whole stands in a vessel of ammonium chloride solution in which is also a zinc rod. The zinc dissolves as before, forming zinc ions, while the ammonium ions are discharged at the carbon pole. After discharge they break up into ammonia and hydrogen, the former remaining dissolved while the latter is

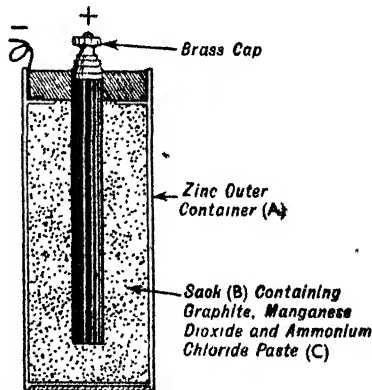


FIG. 15.4.—Dry Cell

oxidized to water by the manganese dioxide. This oxidation is slow so that the cell may polarize if too big a load is put on it; but it will recover if allowed to rest, and also it will yield a small current for an almost indefinite period.

The modification of the Leclanché cell known as the dry cell is illustrated diagrammatically in Fig. 15.4.

A cylinder of zinc *A* serves both as the negative pole of the cell and as a container. Inside this is a canvas sack *B* containing a moist mixture *C* of carbon, manganese dioxide, ammonium chloride and zinc chloride surrounding a central carbon rod. The action of this cell is exactly similar to that of the preceding cell.

### § 10 Electromotive Force and Chemical Affinity. The Electrochemical Series of the Elements

In the preceding section, the production of the current in a simple cell was seen to be a result of the tendency of zinc in the atomic state to go into solution as zinc ions. In order that a current may be driven round a circuit, there must be a difference of potential between the poles of the cell. Even when no current is flowing, a difference of potential is found to exist and in these circumstances it is called the **electromotive force** or E.M.F. of the cell. Experiment has shown that the value of the E.M.F. of a cell depends upon the nature of the substances forming its poles and, to a lesser extent, on the concentration of the solution in which they are immersed. Thus, for example, a cell consisting of zinc and copper plates immersed in a decinormal solution of sulphuric acid has an E.M.F. of about 1.1 volts; if an iron plate be substituted for the zinc one the E.M.F. falls to about 0.67 volt. It can be shown that, in general, a potential difference exists between the metal and a solution containing ions of this metal in reversible equilibrium with it. When the concentration of the ions is 1 gm.-ion per litre this potential difference is called the **electrode potential** of the metal. By measuring the E.M.F. of a cell composed of such an electrode as one pole and a standard electrode as the other the values of the electrode potentials of the various metals, etc., can be determined. For this purpose the electrode potential of a hydrogen electrode is arbitrarily assumed to be zero. (A hydrogen electrode consists of a plate of platinized platinum (cf. page 222), immersed in a solution of hydrochloric acid containing 1 gm. of hydrogen ion per litre, over which pure hydrogen at 760 mm. is bubbled.) The electrode potential is called positive when the substance of which the electrode is composed is positively charged with respect to the solution, and vice versa.\* Table XIX gives a list of electrode potentials found in this

\* This convention is now being replaced, in some quarters, by the reverse one, i.e. the potential of an electrode is then said to be positive when the *solution* is positively charged with respect to the electrode. This convention is preferred by some since metals such as sodium or zinc which are described as electropositive elements are then given a positive electrode potential.

way, arranged in order of magnitude. A table giving a list of the elements in order of their electrode potentials (such as Table XIX) is known as the **electrochemical series** of the elements.

TABLE XIX.—ELECTRODE POTENTIALS AT 25° C.  
ELECTROCHEMICAL SERIES OF THE ELEMENTS

Element	Electrode potential	Element	Electrode potential
Lithium . . .	-3.02 volts	Silver . . .	+0.799 volts
Caesium . . .	-2.93 "	Mercury (Hg/Hg <sup>++</sup> ) . . .	+0.799 "
Rubidium . . .	-2.925 "	Palladium . . .	+0.82 "
Potassium . . .	-2.925 "	Gold . . .	+1.42 "
Barium . . .	-2.90 "		
Strontium . . .	-2.89 "		
Calcium . . .	-2.76 "		
Sodium . . .	-2.713 "		
Magnesium . . .	-2.38 "	Iodine . . .	+0.536 volts
Aluminium . . .	-1.67 "	Bromine . . .	+1.066 "
Manganese . . .	-1.05 "	Chlorine . . .	+1.358 "
Zinc . . .	-0.763 "	Fluorine . . .	+2.85 "
Chromium (Cr/Cr <sup>+</sup> ) . . .	-0.557 "		
Iron (Fe/Fe <sup>++</sup> ) . . .	-0.44 "		
Cadmium . . .	-0.402 "		
Thallium . . .	-0.33 "		
Cobalt . . .	-0.28 "		
Nickel . . .	-0.23 "		
Tin (Sn/Sn <sup>++</sup> ) . . .	-0.141 "		
Lead . . .	-0.126 "		
Hydrogen . . .	0.000 "		
Bismuth . . .	+0.226 "		
Copper (Cu/Cu <sup>++</sup> ) . . .	+0.34 "		

Examination of this table, in the light of the known chemical behaviour of the elements, shows that it corresponds closely with this chemical behaviour, and affords us some measure of the **chemical affinity** of two substances, that is of their tendency to react.

This quantity is not very easy to evaluate. It may be taken to be proportional to the energy change which takes place when two substances react. Thus, for example, the difference between the energy latent in a mass of sodium and a mass of chlorine on the one hand, and in the mass of sodium chloride formed by their combination, on the other hand, is a measure of the affinity of sodium for chlorine. But it is not easy to be certain of the value of this difference. It is often *approximately* equal to the heat given out in the process, and was at one time thought to be equal to this heat change; but this is now recognized as being not necessarily true since the internal energy of the compound must be taken into account. Nevertheless, the heat change does give a rough measure of the relative affinities of substances, and the results of such investigations are in quite good accord very often with what would be expected from a consideration of the electrochemical series.

It is found also that metals will displace each other from solution in a certain order. The displacement of copper by iron (as, for instance, by immersing a penknife blade in copper sulphate solution) is a very familiar fact. Zinc will similarly displace iron, and magnesium will displace zinc (see page 689). The affinity of magnesium might reasonably be thought to be greater than that of zinc which is in its turn greater than that of iron. Care has to be taken when interpreting the results of displacement experiments to make certain that other factors than the affinities of the elements concerned are not interfering with the results (for example, by causing the evolution of a gas which is removed from the system, etc.). These other disturbing factors will be dealt with more fully in Chapter 17, but when taken into account, a displacement series of the elements can be drawn up, the order of which is virtually the same as that of the electrochemical series.

There is thus a good experimental basis for considering that the electrochemical series gives the relative affinities of the elements and this conclusion can also be justified on theoretical grounds.

When a voltaic cell is in operation producing electrical energy a chemical change is taking place, and the energy liberated in this chemical change is the source of the electrical energy produced. The *quantity* of electricity resulting will depend on the total number of atoms of the material of the plate going into solution which is converted into its compounds (strictly speaking, into its *ion*), but the *potential* at which the electrical energy is produced will be determined by the work given out in building up the compound (in the form of its ions) from its elements.

Suppose  $Q$  faradays of electricity are produced when  $m$  grams of compound are formed in the cell (in the form of ions).

Then by Faraday's first law

$$Q = \frac{m}{e}$$

where  $e$  = electrochemical equivalent.

The work done by the current will be  $EQ$

where  $E$  = potential difference produced.

Let  $W$  = work given out in building 1 gm. of the compound from its elements

Then  $W$  is a measure of the affinity. Since the work given out is the source of the electrical energy, we have

$$mW = EQ$$

$$\text{but } Q = \frac{m}{e}$$

$$\therefore Wc = E$$

that is, the potential difference produced is proportional to the affinity per gram equivalent of compound formed.

Hence it is justifiable to assume that the E.M.F. produced when an element goes into solution forming a compound is a measure of chemical affinity; and the order of the electrochemical series is thus an order of chemical affinities.

### § 11 Overvoltage. Products of Electrolysis

The hydrogen electrode, whose potential is arbitrarily taken as zero, uses platinum as the metal in contact with the hydrogen gas and the hydrochloric acid solution. If a metal other than platinum be used a different potential difference is set up, or, put in another way, a definite potential difference must be applied to such a metal immersed in a normal solution of hydrogen ions in order that evolution of hydrogen gas may just occur. This potential difference (the normal hydrogen electrode again being taken as zero) is known as the **overvoltage** or **overpotential** of the metal. Table XX shows the values of the overvoltage of some metals.

TABLE XX

Metal	Overvoltage
Polished platinum . . . .	0.09 volt
Silver . . . . .	0.15 "
Copper . . . . .	0.23 "
Lead . . . . .	0.64 "
Zinc . . . . .	0.70 "
Mercury . . . . .	0.78 "

This property has a bearing on the products obtained as the result of electrolysis. For example, if a potential difference of less than 0.78 volts be applied to a mercury cathode immersed in a normal solution of hydrogen ions no hydrogen will be evolved. Furthermore, if a solution containing both hydrogen ions and lead ions be electrolysed, using a lead cathode, the lead ions will be discharged and lead will be deposited in preference to hydrogen since the potential difference which must be applied to discharge lead ions is 0.126 volt (Table XIX) and that necessary to liberate hydrogen on a lead electrode is 0.64 volt (Table XX).

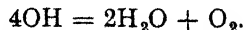
### Products of Electrolysis

The substances evolved from, or deposited on, the electrodes are not always the discharged ions of the principal solute. Thus, while the electrolysis of fused sodium chloride yields sodium at the cathode and chlorine at the anode, if an aqueous solution of common salt be used hydrogen appears at the cathode along with sodium hydroxide in solution. Further, the nature of the electrodes plays a part, as, for example, in the electrolysis of copper sulphate solution where oxygen is evolved at a platinum anode, whereas a copper anode dissolves and no gas is liberated.

These effects were formerly ascribed to secondary reactions. It was supposed that, in the electrolysis of aqueous sodium chloride solution, sodium ions are first discharged at the cathode, forming free sodium, which then acts upon the water with the liberation of hydrogen and formation of sodium hydroxide solution. The electrolysis of copper sulphate solution was similarly explained by supposing that, after discharge, the sulphate ions attack the electrode, if of copper, reforming copper sulphate; or the water, if the electrode be platinum, liberating oxygen.

These explanations are now felt to be unsatisfactory since they imply that sodium ions at first present in solution are discharged and that the metallic sodium attacks the water reforming sodium ions. A similar difficulty attends this explanation of the electrolysis of copper sulphate. These phenomena are now explained on the basis of the known values of the electrode potentials and of overvoltages. Thus, in the electrolysis of sodium chloride solution, sodium ions, chlorine ions, hydrogen ions and hydroxyl ions are present in the solution. At the cathode hydrogen ions are discharged in preference to sodium ions because hydrogen stands below sodium in the electrochemical series (i.e., it has a smaller electrode potential); in other words the tendency of hydrogen ions to gain electrons is greater than that of sodium ions.

The effects observed in the electrolysis of copper sulphate with a copper anode are similarly a consequence of the very low electrode potential of copper, which can become a copper ion more easily than either hydroxyl ions or sulphate ions can be discharged. With a platinum anode the hydroxyl ions, being less electronegative than sulphate ions, are discharged in preference; oxygen then results from the reaction



The influence of overvoltage is seen in the electrolysis of common salt using a mercury cathode as in the Kellner-Solvay Cell (page 532). The high overvoltage of mercury prevents the discharge of hydrogen ions, which are present in only small quantity, and so sodium ions are discharged instead and go into solution in the mercury, forming sodium amalgam.



## CHAPTER 16

# THERMO-CHEMISTRY

Sine igni nihil operamur.—C. GLASER.

Heat and cold are Nature's two hands by which she chiefly worketh —F. BACON.

Each element as well as each compound embodies a distinct and invariable amount of energy as well as a distinct and invariable quantity of matter, and thus energy is a constitutive and essential part of the existence of such element or compound.—J. B. SIELLO.

### § 1 Chemical Energy

IN the discussion of the criteria of chemical change (Chapter 4, page 57) we saw that such changes are in general associated with changes of energy in the form of heat, light or electricity. These energy changes are most often noticed in the form of the *heat evolution* or *heat absorption* accompanying a reaction, but on occasion other forms of energy are liberated.

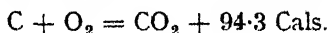
The study of the heat changes accompanying chemical action is often referred to as the study of **thermo-chemistry**.

All chemical substances are associated with a certain amount of intrinsic energy, which is liberated, usually, as we have seen, in the form of heat, to a greater or less degree when it undergoes a chemical reaction. Any chemical system, whether comprising a single substance or a group of substances, contains a definite amount of energy depending upon the mass, chemical nature and physical conditions of the system. This remains constant so long as the system remains unaltered, but when a reaction takes place the products of the reaction will constitute a new chemical system of different intrinsic energy. What these intrinsic energies (i.e., the absolute value of the total energies) are we do not know, but the *change* in total energy when the initial system passes into a new system can be determined, and if no external work is done the decrease in intrinsic energy will be equal to the heat evolved, or vice versa.

### § 2 Heat of Reaction

Experiment shows that the heat effect associated with any given chemical change has a constant value for a given quantity of the reactants. When this value is expressed as the quantity of heat liberated (or absorbed) during the reaction of the gram-molecular quantities of the reacting substances as indicated by the equation for the reaction, it is known as the **Heat of Reaction**. The amount of heat is usually expressed in kilogram-calories (represented by Cals.);

a kilogram-calorie being the amount of heat required to raise the temperature of one kilogram of water by  $1^{\circ}\text{C}$ . The heat of reaction is often included in the equation, as, for instance:



which indicates that 12 grams of carbon combine with 32 grams of oxygen with the formation of 44 grams of carbon dioxide and with the liberation of 94.3 Calories of heat.

The heat of reaction will, of course, depend upon the physical state of the reacting substances and of the products of reaction, and unless there is no possibility of doubt, this ought to be indicated when giving the value of the heat of reaction. In practice, it is usual to quote heats of reaction calculated on the assumption that all the substances concerned are in that physical state characteristic of them at normal temperature and pressure.

Allowance must be made in calculating the heat of reaction as defined above from observed values when gases are liberated (or absorbed) for the external work thus done, which will be equivalent to some of the heat evolved by the reaction. When a gas is formed under atmospheric pressure, the external work done per gram-molecule of gas is given by  $PV = RT$ . Since  $R$  in this case has the value of 1.988 gram-calories, it follows that for each gram-molecule of a gas formed in a reaction under atmospheric pressure there must be added to the measured heat of reaction 1.988  $T$  gram-calories ( $T$  being expressed on the absolute scale). Thus, to quote an example mentioned by Findlay, the reaction  $\text{Zn} + \text{H}_2\text{SO}_4\text{aq} = \text{ZnSO}_4\text{aq} + \text{H}_2$  gives out a measured quantity of heat equal to 34.2 Cals. at  $16^{\circ}$ . For this temperature,  $RT = 575 \text{ gm.-cals.}$ , or 0.575 Cal., so that the real heat of reaction is  $34.2 + 0.575 = 34.775 \text{ cals.}$  Conversely, if gases are absorbed during a reaction, a quantity 1.988  $T$  gm.-cals. must be subtracted from the measured value to give the true heat of reaction.

The quantity of heat liberated or absorbed when one gram-molecule of a compound is formed from its elements is called the **heat of formation** of the compound. Similarly the quantity of heat liberated when one gram-molecule of an element or compound is completely oxidized is called the **heat of combustion**.

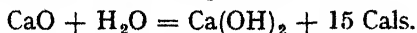
### § 3 Hess's Law

As stated in the previous section, a certain definite heat change is associated with each particular chemical change. That the value found for this heat of reaction is independent of the way in which the reaction is carried out was further shown by G. M. Hess who, in 1840, measured the heat developed during the formation of a compound made in several different ways and came to the conclusion that **the amount of heat evolved during the formation of a given compound is the same whether the compound is formed directly all at once or slowly**

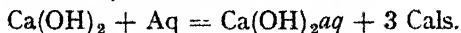
in a series of intermediate stages. This is called **Hess's Law**. The principle may be illustrated by making calcium chloride by the action of quicklime on dilute hydrochloric acid. It is found that



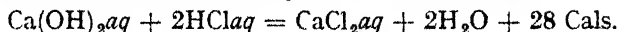
Instead of this, first slake the quicklime, and



Dissolve the calcium hydroxide in water, and



Mix the lime water with dilute hydrochloric acid, and



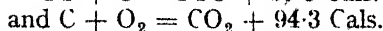
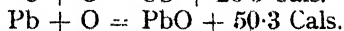
These three steps in the formation of the solution of calcium chloride give a total  $28 + 3 + 15 = 46$  Cals. as the heat of formation. The same result was obtained by the direct action of the dilute acid on quicklime. A number of experiments made on similar lines have shown that (1) **the heat of formation of a compound is independent of its mode of formation**; and (2) **the thermal value of a reaction is independent of the time occupied by the change**.

It follows from Hess's Law that if the heat of formation of carbon dioxide be:  $\text{C} + 2\text{O} = \text{CO}_2 + 94.3$  Cals.; and  $\text{CO} + \text{O} = \text{CO}_2 + 68$  Cals., we have

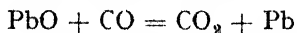
$$(\text{C} + 2\text{O}) - (\text{CO} + \text{O}) = 94.3 - 68 \text{ Cals.}$$

Consequently, the heat of formation of carbon monoxide is:  $\text{C} + \text{O} = \text{CO} + 26.3$  Cals. This illustrates the fact that **the thermal value of a reaction is the sum of the heats of formation of the final products of the reaction less the heats of formation of the reacting substances**. This corollary to Hess's Law is valuable because it enables the heat of formation of a compound from its elements to be computed when a direct determination is either impracticable or very difficult. Similarly the thermal value of a reaction can be deduced when the heats of formation of the different substances which take part in the reaction are known.

Thus, if we know that



it follows that the heat of the reaction:



is given by  $94.3 - (26.3 + 50.3) = 17.7$  Cals.

\* The convention is now adopted by some in which a reaction in which heat is evolved is written with a minus sign to indicate that the products of the reaction contain less total energy than the initial substances. The older system is preferred by many since items on the right-hand side of an equation represent substances (and heat) produced or evolved in the course of the reaction.

It is to be noted that heats of reaction calculated indirectly in this way may involve considerable error, for although the percentage error in the various experimental values may be quite small, that in their difference may be large.

#### § 4 Measurement of Heats of Reaction

The measurement of the heat of reaction for a given chemical change may be either direct or, making use of Hess's Law as explained above, indirect. But in either case we are dependent finally on actual measurements of the heat change inherent in some reaction or reactions, so that methods of determining these are of importance.

The value of the heat of reaction for a change which takes place in solution can be found by ordinary calorimetric methods. Thus, to determine, for example, the heat of neutralization of a dilute solution of hydrochloric acid and sodium hydroxide a known volume of sodium hydroxide solution of definite concentration is placed in a calorimeter. An equivalent quantity of hydrochloric acid solution is contained in a separate vessel and both solutions are brought to the same temperature. This temperature is noted, and the acid is then added rapidly to the alkali and the mixture well stirred. The rise in temperature is measured by means of a delicate thermometer.

Suppose that  $\frac{1}{n}$ th normal solutions were used and that  $v$  c.c. of each were used while the rise in temperature was  $t^\circ$ . Let  $w$  be the water equivalent of the calorimeter. Assuming that the solutions were sufficiently dilute for the specific heats and densities to be taken as unity without serious error, we have:

Heat produced in the reaction =  $(w + 2v)t$  Cals.

Now 1 gram-molecule of each substance is contained in  $n$  litres. Therefore, the heat produced on mixing  $n$  litres of each solution would be

$$\frac{(w + 2v)t \times 2000n}{2v} \text{ cals.} = \frac{(w + 2v)tn}{v} \text{ Cals.}$$

$$= \text{heat of neutralization.}$$

When the heat evolved in a reaction under investigation is very large, or where large quantities of gaseous products result, special methods have to be used.

As an example of these the use of the bomb calorimeter may be cited, this being particularly suitable for the measurement of *heat of combustion*, i.e., the heat produced when a combustible substance, as, for example, carbon, combines with oxygen. This process consists in burning a known weight of the substance in compressed oxygen in a closed steel vessel known as the *bomb*.

The bomb used is illustrated diagrammatically in Fig. 16.1.

It consists of a steel vessel with a tight-fitting lid which is screwed down on to a lead washer. The substance to be burned is weighed and placed in the crucible  $T$  and the bomb is filled with oxygen by way of the channel  $K_1$  and the tube  $R$  until the pressure is about 20–25 atmospheres. The bomb is then immersed in a known weight of water contained in a calorimeter. The combustion is started by connecting the spiral of wire (made of platinum or iron)  $a_1, a_2$ , to a source of electricity, thereby raising it to incandescence.

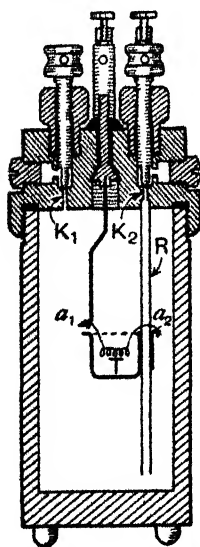


FIG. 16.1.  
Bomb Calorimeter

The temperature of the water in the calorimeter is then taken every minute so that a cooling correction may be applied to the maximum temperature recorded. The heat of combustion of the substance, at constant volume, can then be calculated, the water equivalent of the bomb being known.

### § 5 Endothermic and Exothermic Compounds

We are apt to think of the formation of a compound from its elements as being accompanied by the *evolution* of heat, because many familiar instances where this is true present themselves to our minds. But it is by no means always the case, and many substances are known which, if they are formed by combination of their constituent elements, *absorb* heat. A common example of this class of substance is the gas acetylene. Compounds which are formed with evolution of heat are called **exothermic** compounds; while those which are formed with absorption of heat are known as **endothermic**. Reactions are referred to similarly as exothermic or endothermic reactions, according as they are attended with evolution or with absorption of heat.

The knowledge as to whether a given compound is exothermic or endothermic is of considerable importance, for it enables us to predict its stability under different temperature conditions. An endothermic compound will contain more energy than the elements from which it is made, and it follows from Le Chatelier's Principle (see page 248), as shown in the next chapter, that such a compound will require a high temperature for its formation and will be stable at high temperatures rather than low ones. Conversely, exothermic compounds are stable at low temperatures, but not at high temperatures.

Familiar examples of endothermic compounds are acetylene, oxides of nitrogen and ozone. Common exothermic substances are carbon monoxide and carbon dioxide, and water.

### § 6 Heats of Linkages. Bond Energies

It was pointed out earlier in the present chapter that we have no means of determining the total intrinsic energy either of reacting substances or of the product of a reaction, but only the difference between them. In stating the heats of reaction and of formation of compounds, we have accordingly taken as our datum line the elements themselves.

In certain cases, however, this will lead to errors and discrepancies, for the molecular condition of different elements is very different. Thus, carbon in the form of a diamond is a complicated structure (*cf.* page 368) of atoms joined together by covalent bonds, and when this is burnt to carbon dioxide these bonds will have to be severed and energy will be used up in the process. This supposition is confirmed by the fact that the heat of combustion of amorphous carbon is greater than that of diamond.

Similarly in any combustion the oxygen molecule has to be broken down into its atoms before combination can take place, and again energy will be required. Modern research in thermo-chemistry has accordingly been directed to the determination of the heat changes involved in the formation of various linkages and these are now known with a fair degree of accuracy.

These values likewise represent the energy required to break a particular bond

and hence are known as *bond energies*. Some representative values are (in kilogram. calories per gram-molecule)

H - H	103.2 Cals.	C - H	98.2 Cals.
O - O	34.0 "	C - Cl	78.0 "
Cl - Cl	57.1 "	Cl - H	102.1 "
C - C	80.0 "	N - H	92.2 "
C = C	145.0 "	O - H	109.4 "
C $\equiv$ C	198.0 "		

## CHAPTER 17

# CHEMICAL EQUILIBRIUM AND THE VELOCITY OF REACTIONS

I often say that if you can measure that of which you speak, and can express it by a number, you know something of your subject, but if you cannot measure it, your knowledge is meagre and unsatisfactory.—LORD KELVIN.

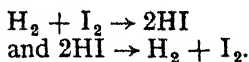
. . . The streaming atoms  
Fly on to clash together again and make  
Another and another state of things  
For ever. . .

*Rejected Addresses*

### § 1 The Extent to which Reactions Proceed

It is well known that reactions do not all proceed instantaneously or to completion, although many do both. Thus, for example, if we mix aqueous solutions of sodium chloride and silver nitrate of equivalent concentration, we immediately see the formation of a precipitate of silver chloride, and almost the whole of the silver and of the chlorine are removed from the solution, the slight trace of either remaining in solution being due to the slight, though measurable, solubility of silver chloride.

There are, however, reactions which proceed relatively slowly, and often these do not proceed to completion. Thus, for example, when a mixture of equal volumes of iodine vapour and hydrogen is passed through a red-hot tube, or better, over heated finely divided platinum or platinized asbestos, or charcoal, some hydrogen iodide, HI, is formed. If hydrogen iodide gas be treated in a similar way, some iodine and hydrogen are produced. In either case, if the temperature of the tube be  $440^{\circ}$ , we have approximately 80 per cent of hydrogen iodide, and 20 per cent of a mixture of equal volumes of iodine and hydrogen. The only apparent effect of the catalytic agent—platinized asbestos, etc.—is to accelerate the reaction, and if these agents be absent, the time required to make 80 per cent of hydrogen iodide from the mixture of hydrogen and iodine is much longer. Once this proportion of hydrogen iodide has been formed, the composition of the exit gases remains unchanged, however long the mixture may be heated at  $440^{\circ}$ , with or without the catalytic agents. This is due to the fact that although at this temperature hydrogen and iodine will combine together to form hydrogen iodide, this hydrogen iodide, when formed, has in its turn a tendency to decompose into hydrogen and iodine. So that, in fact, we have two reactions occurring simultaneously, which may be represented thus:



This reaction is therefore spoken of as a **balanced** or **reversible reaction** and is usually represented by replacing the equality sign in the equation by two arrows, thus:

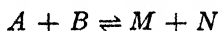


When, as in the above example, the gases have been maintained in contact for a sufficient length of time, a state of **equilibrium** is set up between the hydrogen and iodine on the one hand and the hydrogen iodide on the other.

## § 2 The Law of Mass Action

The condition of equilibrium, under given conditions (in particular at a given temperature) in the case of a balanced reaction can be deduced by the application of the **Law of Mass Action** which was first enunciated clearly by Guldberg and Waage in 1867, in consequence of which it is sometimes known as Guldberg and Waage's Law. This states that *the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances*. The phrase "active mass" is perhaps strange to our ears; by it, Guldberg and Waage meant what we term the molecular concentration of a substance.

We can apply this law to determine the condition of equilibrium in an homogeneous reaction in the following way. Consider the reaction:



and let  $[A]$  and  $[B]$  respectively denote the concentrations of the substances  $A$  and  $B$ , expressed in gram-molecules per litre. Similarly, let  $[M]$  and  $[N]$  respectively denote the concentrations  $M$  and  $N$ . From the above law the speed of the reaction is proportional to the concentrations of the reacting substances, that is, the velocity of the reaction  $A + B$  is equal to  $k[A][B]$  where  $k$  is a constant. Similarly, the velocity of the reaction in the opposite direction will be proportional to  $[M][N]$  or equal to  $k'[M][N]$ . In these expressions  $k$  and  $k'$  are constants, called *velocity constants* (see § 7 below). When the conditions are such that the velocities of these two reactions are identical, a state of equilibrium will result. We then have

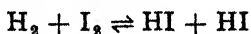
$$k[A][B] = k'[M][N]$$

$$\text{i.e., } \frac{[M][N]}{[A][B]} = \frac{k}{k'} = K \text{ (another constant).}$$

So that at equilibrium we conclude that the product of the concentrations of the substances on the right-hand side of the equation, divided by the product of the concentrations of the substances on the left-hand side of the equation, is a constant at a given temperature. This constant is known as the *equilibrium constant* for the reaction at this temperature.



Some examples of the application of these conclusions to actual reactions may now be given. The simplest cases are those which occur in gaseous systems, and the hydrogen—iodine—hydrogen iodide equilibrium already referred to is a good example of this type. The reaction is represented by the equation:



from which we conclude that the condition of equilibrium at a given temperature will be given by

$$\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2}$$

Suppose that  $a$  gram-molecules of hydrogen and  $b$  gram-molecules of iodine are heated together, the total volume being  $v$  litres. Let the amount of hydrogen iodide present at equilibrium be  $2x$  gram-molecules,  $a - x$  gram-molecules of hydrogen and  $b - x$  gram-molecules of iodine having combined. Then we have, at equilibrium:

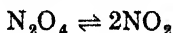
$$[\text{H}_2] = \frac{a - x}{v}, [\text{I}_2] = \frac{b - x}{v} \text{ and } [\text{HI}] = \frac{2x}{v}$$

$$\therefore K = \frac{\left(\frac{a - x}{v}\right)\left(\frac{b - x}{v}\right)}{\left(\frac{2x}{v}\right)^2} = \frac{(a - x)(b - x)}{4x^2}$$

The volume term  $v$  is thus seen to cancel out in this expression, from which it follows that the equilibrium in this case is not affected by change of volume, and consequently change of pressure is also without effect. (Cf. Le Chatelier's Principle, page 248.)

This equilibrium was extensively investigated by Bodenstein (1897) and his results confirm these conclusions. In addition, he showed that the same equilibrium is set up whether we begin with hydrogen and iodine, or with hydrogen iodide.

Another interesting and instructive example of equilibrium in the gaseous state is afforded by nitrogen peroxide. This gas undergoes dissociation at moderate temperatures, as indicated by the equation:



(cf. page 466). If we apply the law of mass action here we have

$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = K$$

Now supposing we have  $a$  gram-molecules of  $\text{N}_2\text{O}_4$  in a volume of  $v$  litres, and that  $x$  gram-molecules have dissociated, thus forming  $2x$  gram-molecules of  $\text{NO}_2$ . Then,

$$\frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)} = K$$

$$\text{i.e.,} \quad \frac{4x^2}{(a-x)v} = K$$

Here  $v$  the volume appears in the expression for the equilibrium constant, and hence the concentrations of the two types of molecule at equilibrium are dependent upon the volume, and consequently upon the pressure. Further, since  $v$  appears in the denominator, it follows that if we increase the volume (or decrease the pressure) of the system there will be an increase in the proportion of  $\text{NO}_2$  molecules present, and vice versa. These conclusions are borne out by the results of experimental investigations of this equilibrium.

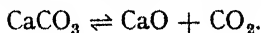
Generalizing from the two examples so far discussed, we see that where a reaction in the gaseous state takes place without change of volume, pressure is without influence on the equilibrium; conversely, reactions which involve a change in volume have the equilibrium altered by changes in pressure.

Homogeneous reversible reactions are not confined to the gaseous phase, but may take place in solution. Since almost all reactions in solution between inorganic substances are ionic in nature, the equilibria involved are largely bound up with those of the ions themselves. The application of the Law of Mass Action to electrolytes is discussed in the next chapter. The most familiar examples of balanced reactions in solution are, therefore, those of organic compounds and consequently fall outside the scope of a text-book of inorganic chemistry.

### § 3 The Law of Mass Action and Heterogeneous Systems

So far we have considered only balanced reactions which take place in one phase, that is, homogeneous reactions. There are, of course, a great many reactions which take place between substances in different phases, and these are known as heterogeneous reactions. Numerous reversible, heterogeneous reactions are known, and it is necessary now to consider how far the law of Mass Action can be applied to such cases.

Let us consider the familiar reaction of the decomposition of calcium carbonate by heat—a well-known example of a reversible reaction (cf. page 697) which may be represented by the equation:



If all three substances were in the form of vapour we could apply the Law of Mass Action to the equilibrium and should have the result:

$$\frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]} = K$$

where  $[CaO]$ ,  $[CO_2]$  and  $[CaCO_3]$  are the concentrations of calcium oxide, carbon dioxide, and calcium carbonate respectively. Some solids have a measurable vapour pressure and, as in the case of liquids, the vapour pressure is fixed at a constant temperature. Therefore we assume that calcium oxide and carbonate, which are solids under the conditions of the experiment, have a real, though very small, vapour pressure. The partial pressure of a given gas in a mixture of gases is proportional to its volume. By Avogadro's hypothesis the volume of a gas in a mixture is proportional to its molecular concentration. Therefore we can express the concentrations of substances in the vapour phase in terms of their partial pressures, since these are proportional to the concentrations. The expression for the equilibrium constant then becomes:

$$\frac{p_{CaO} \times p_{CO_2}}{p_{CaCO_3}} = K$$

where  $p_{CaO}$ ,  $p_{CO_2}$  and  $p_{CaCO_3}$  are the partial pressures of calcium oxide, carbon dioxide and calcium carbonate respectively. The vapour pressures of the solids will be constant, at a given temperature, so long as these solids are present; hence in the present instance  $p_{CaO}$  and  $p_{CaCO_3}$  are constants, so that we have:

$$p_{CO_2} = K.$$

The system, therefore, is at equilibrium at a given temperature when the partial pressure of the carbon dioxide present has the required fixed value. This result is confirmed by experiment which shows that there is a certain fixed **dissociation pressure** of carbon dioxide for each temperature. The same conclusion can be deduced from the application of the phase rule (see page 185). We have two components\* existing in three phases; hence  $F = 2 - 3 + 2 = 1$ , or the system possesses one degree of freedom.

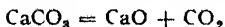
We may thus legitimately conclude that the assumption made in applying the Law of Mass Action to a heterogeneous system is justified, and hence conclude that in such systems *the active mass of a solid is constant*.

Another common example to which the same considerations apply is that of the action of steam on red-hot iron, which is represented by the equation:



Assuming that the active masses of the solids are constant, we have, using the same notation as before:

\* Three different *substances* (calcium carbonate, calcium oxide and carbon dioxide) are present but they are not all to be considered components (in the Phase Rule sense) since they are not all mutually independent. If *two* of them are chosen the composition of the third is defined by the equation



so that the number of components is two.

$$\frac{(p_{H_2O})^4}{(p_{H_2O})^4} = K$$

i.e.,

$$\frac{p_{H_2O}}{p_{H_2O}} = K'$$

Again, this result is borne out by experiment, so that the assumptions on which it is based seem to be justified.

#### § 4 Dissociation of Salt Hydrates

Similar considerations apply to the dehydration of salts which contain water of crystallization.

Consider the case, for example, of hydrated copper sulphate— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . When this is heated it passes, first, into  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , then into  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , and finally into anhydrous copper sulphate. The first of these stages may be represented by the equation:



Applying the principles employed in the preceding section, we have:

$$\frac{p_1 \times p_2^2}{p_1} = K$$

when  $p_1$ ,  $p_2$  and  $p_3$  are the partial pressures of the pentahydrate, the trihydrate and of water vapour respectively. But, as we have said, so long as the solids remain, their vapour pressures will be constant, so that  $p_1$  and  $p_2$  are constant; hence the expression for the equilibrium becomes:

$$\text{i.e.,} \quad \begin{aligned} p_3^2 &= K \\ p_3 &= \sqrt{K} = K'. \end{aligned}$$

Again, we see that at a given temperature a particular pressure of the water vapour present is necessary for equilibrium. This result again is deducible from Phase Rule considerations.

When one of the hydrates has disappeared, a new equilibrium will be set up, and the partial pressure of water vapour will have a different value, but will again remain constant so long as the same two hydrates are present.

These conclusions are upheld by experimental results which show that in the dehydration of copper sulphate the pressure remains constant at the value for the dissociation pressure of the pentahydrate for some time, and then drops *suddenly* to that of the next hydrate. The graph in Fig. 17.1 shows the variation in vapour pressure of copper sulphate in a dehydration experiment.

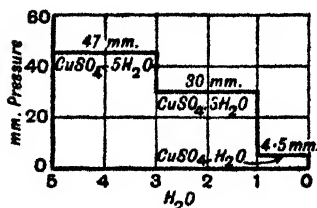


FIG. 17.1.

Vapour Pressure Curves of the Hydrates of Copper Sulphate

Consideration of these results enables us further to account for the phenomena of **efflorescence** and **deliquescence**. Thus, if the partial pressure of the water vapour present in the air at a given time is *less* than the dissociation pressure of a particular salt hydrate, the latter will give up water vapour, thus losing part (or all) of its water of crystallization. This is the phenomenon known as **efflorescence**. If the partial pressure of water vapour is *greater* than that of the hydrate, the salt will absorb moisture from the atmosphere. This is what is known as **deliquescence**.

These conclusions are illustrated by Table XXI. The partial pressure of water vapour in the atmosphere is normally in the region of 10 mm. of mercury, and rarely exceeds 15 mm.

TABLE XXI.—VAPOUR PRESSURES OF HYDRATES

Salt	Vapour pressure mm.	Property
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	3.2	Deliquescent
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	6.0	Deliquescent
$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	27.8	Efflorescent
$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	24.2	Efflorescent

### § 5 The Effect of Pressure and Temperature on Equilibria— Le Chatelier's Principle

The application of the Law of Mass Action to homogeneous systems in equilibrium leads to the conclusion that the equilibrium will be unaffected by pressure if the reactions occurring take place without change of volume (see § 2, page 243). Also, where change of volume does take place, increase of pressure will cause the equilibrium to shift in that direction, which is attended with a decrease in volume, and vice versa. These conclusions, further, have been verified by experiment and hence it may be said that in general, *when a system is in a state of physical or chemical equilibrium, an increase of pressure favours the system formed with a decrease in volume; a reduction of pressure favours the system formed with an increase in volume; and a change of pressure has no effect on a system formed without a change in volume.*—**G. Robin's Law** (1879). Thus we have a qualitative generalization giving the effect of *pressure* on equilibria.

Similar considerations apply to the influence of temperature, but we cannot get any direct guidance from the Law of Mass Action in this case. Experience shows that most reactions proceed at an increased speed with increase of temperature, but that no two reactions are affected to the same extent. In consequence it follows that, since equilibrium is established when the speeds of the forward and back reactions are equal, if these speeds are changed by rise in temperature to a different extent, then the position of the equilibrium will be moved. How can we predict in which direction it will move?

By analogy with the effect of pressure which we have correlated with the change in volume in the reaction, it might be expected that the effect of temperature could be related to the heat change which (Chapter 16) accompanies all reactions. By analogy also, a rise in temperature would be expected to promote those reactions which proceed with the absorption of heat, and vice versa. Experiment bears out this supposition and so, generalizing, it may be said that: *When a system is in physical or chemical equilibrium, a rise of temperature promotes the formation of those products which are formed with an absorption of heat; a rise of temperature resists the formation of those products formed with an evolution of heat; and a change of temperature has no effect on the equilibrium of reactions thermally neutral.*—J. H. van't Hoff's Equilibrium Law (1884).

These two generalizations are combined in that made by Le Chatelier (1888) and known as **Le Chatelier's Principle**, which states that: *If a change takes place in one of the factors, such as temperature or pressure, under which a system is in equilibrium the system will tend to adjust itself so as to undo the effect of that change.*

This important principle enables us qualitatively to predict the influence of external conditions upon equilibria, and its application to some important cases may now be discussed.

As an example of an equilibrium unaffected by pressure, in which the effect of temperature alone can, therefore, be studied, we may take the synthesis of nitric oxide from its elements. This reaction may be represented:



so that the formation of nitric oxide, while involving no change in volume, is attended with the *absorption* of a large quantity of heat. The amount of nitric oxide present at equilibrium will thus, according to the Principle of Le Chatelier, be unaffected by changes of pressure, whereas increase of temperature should cause the formation of a larger proportion of nitric oxide. These conclusions were confirmed by the work of Nernst, and the following figures indicate the kind of result obtained:

Temperature . . .	1811°	2033°	2195°	3000°	3200°
Percentage of NO at equilibrium . . .	0.37	0.64	0.997	4.5	5.0

The Birkeland-Eyde process for the Fixation of Nitrogen was based upon these facts (see page 448).

It is not possible to find a reaction for discussion in which the pressure effect can be isolated, because reactions always involve heat changes; but the combined influence of temperature and pressure can be studied in the important reaction between nitrogen and hydrogen used in the synthesis of ammonia by the Haber Process (see page 429).

This reaction is represented:



which indicates that the formation of ammonia from its elements is attended by a large reduction in volume (the volume is halved); and the evolution of a considerable quantity of heat. Consequently, increase of pressure will favour, and increase of temperature will hinder, the production of ammonia. This is borne out by Table XXII which shows the percentage of ammonia at equilibrium under different conditions, as determined by Larson and Dodge (1923).

TABLE XXII.—EQUILIBRIUM BETWEEN NITROGEN, HYDROGEN AND AMMONIA  
Percentage of Ammonia

° C.	Pressure in Atmospheres					
	10	30	50	100	300	600
350°	7.35	17.80	25.11			
400°	3.85	10.09	15.11	24.91		
450°	2.04	5.80	9.17	16.35	35.5	53.6
500°	1.20	3.48	5.58	10.40	26.2	42.1

The effects of temperature and pressure are both clearly shown by these figures and are in accordance with Le Chatelier's Principle. The application of these results to the commercial synthesis of ammonia is discussed in Chapter 23.

### § 6 The Velocity of Reactions

So far we have considered the conditions for the attainment of equilibrium in balanced reactions, and, although we assumed that these were dependent upon the speeds of the opposing reactions, we have not yet discussed these reaction velocities themselves.

The Law of Mass Action, stated on page 242, is primarily a generalization concerning the *velocity* of chemical reactions, although so far we have only applied it to the case of equilibria (recognizing that these equilibria are kinetic in nature). But it is important to consider its application to reaction velocities themselves and the methods by which they may be investigated experimentally, especially as the law does not tell us anything about the *absolute* velocity of any given reaction, although it gives us valuable information about the way in which the velocity is altered by changes in the proportions of the reacting substances.

Although our knowledge is steadily increasing, we are still somewhat uncertain as to the *exact mechanism* of chemical change, but the Kinetic Theory affords a useful picture of the sort of considerations involved. According to the Kinetic Theory, we imagine that a gas consists principally of empty space in which the molecules are continuously moving, colliding with each other and the walls of the vessel, and rebounding. A liquid we conceive as a collection of molecules, also in motion, colliding and rebounding with each other, but having

very little free space between them; held together by molecular attraction and only prevented from close and continuous contact by their motion. A solid we believe to be composed of atoms or molecules in ceaseless *vibration*.

It is a reasonable assumption that, for a chemical reaction to occur between two substances, the reacting molecules should come into contact, or at least approach each other very closely, so that it would be expected that reactions between two solids would be very rare; while reactions involving liquids and gases, either with other liquids or gases, or with solids, should occur frequently. This is, of course, what is found experimentally; non-volatile solids react with each other as a rule only if subjected to very heavy pressure.

The older chemists did not believe that solids could react chemically, but W. Spring claims to have formed sulphides and arsenides of metals by the alternate compression and filing of intimate mixtures of the metals with sulphur and arsenic respectively. Other reactions brought about, according to Spring, by pressure, are those between sodium carbonate and barium sulphate; potassium nitrate and sodium acetate; mercuric chloride and potassium iodide, etc. There is no reason to doubt that combination did occur in these cases, even if it did not go to completion; and this fact shows that the molecules of solids can be brought close enough for chemical union.

On this assumption, that chemical reaction involves a close approach between the reacting molecules, we should expect that any condition tending to increase the number of collisions between molecules would also increase the rate of reaction. Theoretically, the number of these collisions can be increased in two ways (assuming, for the moment, a constant temperature). These are:

- (1) the average distance between the molecules can be decreased by increasing the pressure upon the system;
- (2) the number of molecules of each kind present can be increased.

If two molecules are to react they must (on our assumption) collide. The chances of *each* molecule doing so are doubled if the total volume of the system is halved; hence the chances for *both* are multiplied by four, i.e., as the square of the pressure. Similarly, in a reaction involving  $n$  molecules, the chances of the appropriate juxtaposition of molecules will vary as the  $n$ th power of the pressure. The rate of reaction will thus vary also according to the  $n$ th power of the pressure.

Similarly, if we require two molecules of different kinds to meet (and react) the chance of a particular molecule being at a particular spot is proportional to the number of molecules of that kind within reach. So also with the second molecule, and so with  $n$  molecules. Hence, there is a logical reason for the dependence of reaction velocity upon concentration.

These considerations are summed up in the Law of Mass Action which, as given on page 242, states that *the rate of a chemical*



*reaction is proportional to the product of the active masses of the reacting substances.*

For a long period before the Law of Mass Action had been enunciated by Guldberg and Waage it was known that the progress of a reaction is affected by the amount of reacting substances present. Thus, Wenzel in 1777 investigated the solution of zinc and copper in acids and recognized the relationship in this case between the rate of reaction and concentration. He found that if an acid of a given concentration reacts with one unit of metal per hour, an acid of half that concentration will take two hours. Similarly, Wilhelmy in 1850 investigated the inversion of cane sugar and expressed his results in a mathematical relation between the rate of inversion and the concentration, and a more general investigation, along similar lines, was undertaken by Harcourt and Esson, 1866, just before Guldberg and Waage published their conclusions embodied in the Law of Mass Action as we have it.

### **Influence of Temperature**

In general, almost all chemical reactions proceed at a faster rate when the temperature is raised; sometimes this increase in velocity is very great and on the average it is found that the reaction velocity is doubled by a rise in temperature of  $10^{\circ}\text{C}$ . This effect is *qualitatively* in harmony with what would be expected on the basis of the Kinetic Theory, for according to this theory (cf. Chapter 2, § 11) a rise in temperature causes an increase in the velocity of the molecules, and hence of the number of collisions between them. This increase can readily be calculated, but comes out at a figure which rarely exceeds one-fifth of that which is found by experiment, and is usually only one-tenth or less.

The explanation of this discrepancy is believed to be the fact that not all the collisions between molecules are fruitful collisions in the sense of bringing about reaction. Thus Bodenstein, in the course of his investigations on hydrogen iodide, found that at  $283^{\circ}$ , at a concentration of 1 gram-molecule per litre, the number of molecules which react per second is only  $2.1 \times 10^{17}$ , whereas it is calculated that the number of collisions is  $6 \times 10^{34}$ . Some other factor than mere collision is thus involved.

### **§ 7 The Order of Reactions**

The Law of Mass Action states that the rate at which a given chemical reaction proceeds is proportional to the concentrations of the reacting substances. Clearly, therefore, a reaction which involves the interaction of *two* molecules (whether alike or different) will proceed at a rate, the mathematical expression of which will involve *two* factors, and which will therefore have different characteristics as compared with a reaction which involves only the decomposition of a single molecule, or with one in which more than two molecules are essentially involved.

It is convenient to classify reactions on this basis. Reactions which involve only one molecule are termed *unimolecular* reactions or reactions of the *first order*; those which involve two molecules are called *bi-molecular* or second order reactions, and so on. Expressed mathematically we may say that in the reaction:



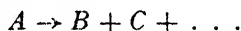
the speed is given by:

$$V = k[A]^l[B]^m[C]^n$$

where square brackets denote "concentration of" and the order of the reaction is the sum of the indices  $l + m + n \dots$ . It is to be observed that the order of a reversible reaction is often different in the reverse direction as compared with the forward direction.

The characteristics of each type of reaction may be discovered from the mathematical expression of the Law of Mass Action.

Thus a **unimolecular reaction** proceeds at a speed proportional to the concentration of the reacting substance. Consider such a reaction as may be represented by the equation:



Suppose that at the beginning of the reaction there are  $a$  gram-molecules of  $A$  present per litre, and that after a time  $t$  has elapsed  $x$  gram-molecules of  $A$  have undergone change so that there are now  $a - x$  gram-molecules of  $A$  remaining. Then, using the notation of the calculus, we have from the Law of Mass Action:

$$v = \frac{dx}{dt} = k(a - x)$$

$$\text{i.e.,} \quad \frac{dx}{a - x} = k dt$$

which on integration gives us:

$$-\log_e (a - x) = kt + C$$

where  $C$  is a constant which can be evaluated from the fact that when  $t = 0$ ,  $x = 0$ . We then have:

$$-\log_e a = C$$

$$\therefore k = \frac{1}{t} \log_e \frac{a}{a - x}$$

$k$  is, of course, a constant known as the *velocity constant* of the reaction. This equation is characteristic of the behaviour of all unimolecular reactions.

A similar reasoning applies to **bimolecular reactions**. Let us consider the reaction



Suppose that, as before, the initial concentration of *A* is *a* gram-molecules, and for simplification let the initial concentration of *B* be the same. Let *x* gram-molecules of each have reacted after time *t*. Then by the Law of Mass Action we have

$$v = \frac{dx}{dt} = k(a - x)^2$$

which on integration gives

$$k = \frac{1}{t} \cdot \frac{x}{a(a - x)}$$

When the initial concentrations of the reacting substances are different the calculation is more complicated, but need not be considered for the present.

Reactions of **higher orders** than the second can be dealt with in a similar manner, but their treatment lies outside the scope of the present work. For their discussion reference should be made to books on physical chemistry.

### § 8 Some Typical Reactions of the First and Second Orders

The investigation experimentally of the velocity with which reactions proceed, with a view to the determination of their *order*, is a matter of considerable importance since it enables us to elucidate the mechanisms of many such reactions. The experimental methods available may be summarized as follows:

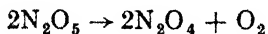
(i) comparison of the experimental data with the formulae deduced as in § 7 to discover which they fit;

(ii) determination of how the time required for the completion of a given fraction of the change depends upon the concentration of the reacting substances (actually a modification of (i) which has much practical convenience);

(iii) determination of the order as in (i) having each reactant separately in excess, in turn, when the sum of the orders so found is the order of the reaction.

#### Unimolecular Reactions

Experiment has shown that truly unimolecular reactions are unexpectedly rare. The best-known case of such a reaction is the decomposition of nitrogen pentoxide. This reaction is usually represented by the equation:

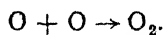


which would lead us to conclude that it is bimolecular. It was investigated by measuring the pressure after various intervals, and also, since it takes place in solution, by measuring the volume of oxygen

evolved when it was allowed to decompose when dissolved in carbon tetrachloride.

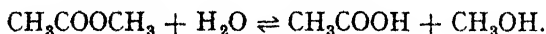
Many reactions appear to be unimolecular when investigated under given conditions, though they are not actually so, and are termed **pseudo-unimolecular reactions**. Many of these are gas reactions which only take place at the surface of a catalyst. (See § 9 for discussion of the phenomena of catalysis.) The walls of the vessel often behave as such a catalyst, in which case the reaction is called a *wall-reaction*, and measurements then frequently indicate a unimolecular reaction where, in fact, the reaction is of another order. (This is further explained in § 9.) In the case of nitrogen pentoxide this point has been investigated and it has been shown that a wall-reaction is not involved.

The fact that the decomposition of nitrogen pentoxide is unimolecular, whereas our equation for the reaction would show it to be of the second order, raises an interesting point. It is evident that two consecutive reactions are involved, one of which is much slower than the other. Whenever we make measurements of reaction velocity in cases where a series of reactions is involved, it is clear that the actual speed observed will be that of the slowest of the reactions occurring. In the case of nitrogen pentoxide, it is likely that the reaction measured is:  $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \text{O}$ , which is followed by the very much faster reaction:



This is an example of the way in which measurements of reaction velocity assist in the elucidation of the mechanism of reactions.

Pseudo-unimolecular reactions have been referred to above, and one type, viz., wall-reactions, mentioned. Another important type of pseudo-unimolecular reaction is that in which one of the reacting substances is present in a concentration relatively so large that its concentration does not change appreciably during the course of the reaction. A case in point, which has been much investigated and which may be mentioned, although it belongs strictly to the study of organic chemistry, is the hydrolysis of esters such as methyl acetate. This reaction is represented by the equation:

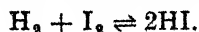


When carried out in dilute solution this reaction appears to obey the unimolecular law since the amount of water present is too large to have its concentration appreciably affected by the reaction. This, incidentally, is the principle underlying method (iii) mentioned above for determining the order of a reaction.

### Bimolecular Reactions

Bimolecular reactions are found to be by far the most common type—reactions of a higher order than two are found to be rare.

The decomposition of ozone into oxygen is an example of a bimolecular reaction; and the reaction between hydrogen and iodine vapour, like the reverse reaction, is a straightforward bimolecular change, as would be expected from the equation:



This reaction was extensively investigated by Bodenstein, whose results indicated that both reactions are indeed bimolecular. The calculations involved are rather more complicated than those given in § 7 since the reaction is a reversible one so that the velocities in both directions must be taken into consideration. It can be shown, however, that the velocity constant for the decomposition of hydrogen iodide, at a given temperature, can be calculated from a knowledge of the amount of hydrogen iodide decomposed in a given time, and the amount decomposed at equilibrium. Similar considerations apply also to the combination of hydrogen and iodine.

The hydrolysis of organic esters (e.g., ethyl acetate) by sodium hydroxide is an example of a straightforward, irreversible bimolecular reaction. The equation for it is:



As the reaction proceeds, caustic soda is used up and so, by determining how much of it remains at stated intervals, the rate of reaction can be measured. For this purpose a dilute solution of ethyl acetate is mixed with an equivalent quantity of sodium hydroxide solution (so that the simplified form of the equation for the velocity of the reaction may be employed) and kept at constant temperature in a thermostat. Measured volumes of the mixture are withdrawn at stated intervals, mixed immediately with excess of standard acid (to stop the reaction) and then titrated back with standard alkali. The amount of alkali used is thus known, and hence the quantity of ester decomposed can be calculated.

TABLE XXIII.—HYDROLYSIS OF ETHYL ACETATE

Time (in minutes)		$\frac{1}{t} \log_e \frac{a}{a-x}$ (unimolecular)	$\frac{1}{t} \cdot \frac{x}{(a-x)}$ (bimolecular)
5	5.76	0.0893	0.0070
15	9.87	0.0640	0.0067
25	11.68	0.0524	0.0069
35	12.59	0.0442	0.0066
55	13.69	0.0352	0.0067

$a = 16.00$  gm.-mols.

Some results obtained in an experiment of this kind are given in Table XXIII, which shows clearly that the bimolecular equation is being obeyed and not the unimolecular.

### § 9 Catalysis

We have seen that the speed at which a chemical reaction proceeds depends upon the physical conditions (i.e., temperature and pressure) under which it takes place, and also upon the concentration of the reacting substances. It is also affected, sometimes to a large extent, by the presence of a small quantity of a foreign substance; that is to say, a substance which does not appear in the equation for the reaction and which can be recovered unchanged chemically after the reaction is over. Such a substance is called a **catalyst** or **catalytic agent** and the general phenomenon of the alteration of the speed of reactions by the presence of catalytic agents is termed **catalysis**. A **catalyst** may thus be defined as **a substance which, when present in comparatively small amount, influences the speed of a chemical reaction without itself undergoing any permanent change in quantity or chemical composition**. Catalysis is generally taken to include the retardation of a reaction, as well as its acceleration, though the more familiar and more practically important cases of catalysis concern the increase in speed.

The usually accepted criteria of catalysis are due to Ostwald and are:

- (i) the catalyst must remain unchanged in amount and in chemical composition at the end of the reaction;
- (ii) only a small amount of catalyst is necessary to produce a measurable effect;
- (iii) the catalyst cannot start a reaction, but only alters the speed of the reaction; it does not alter the final state of equilibrium in a balanced reaction;
- (iv) in a balanced reaction, the catalyst alters the speeds of the forward and back reactions to the same extent.

(The considerations discussed in the earlier sections of this chapter indicate that (iv) is a necessary consequence of (iii).)

These criteria are sometimes true only with certain restrictions or reservations. Thus the requirement that the catalyst should remain unchanged only applies to the chemical composition; in many cases it manifestly does not apply to the *physical* condition. Thus, for example, if in the preparation of oxygen from potassium chlorate using manganese dioxide as a catalyst (see page 333) the manganese dioxide is in the form of small lumps to begin with, it will be found to have become disintegrated to a fine powder in the course of the reaction. Similarly, in the oxidation of ammonia to nitric acid, using platinum as catalyst (see page 448) a smooth platinum surface is found to have become roughened.

The criterion that only a small quantity of catalyst is necessary is usually sound. In fact, the minute quantity of catalyst which will, on occasion, produce a marked effect is one of the most striking characteristics of catalytic phenomena. Thus, in the absence of catalysts, the

oxidation of solutions of sodium sulphite by oxygen takes place only slowly (see page 631). But in the presence of minute traces of copper the speed of the reaction is noticeably increased. Thus, for example, the change in the speed of this reaction brought about by the presence of a concentration of copper ions of only 0.000000636 gm. per litre can be readily detected, and even allowing the water from which the sodium sulphite solution is made up to stand in contact with a copper vessel for 45 seconds, is sufficient to produce a measurable increase in the rate of oxidation.

There has been much controversy as to whether a catalyst can or cannot initiate a reaction. Many reactions, so far as we can judge, do in fact seem to be started by a catalyst, as, for example, some of the observations of Baker on the catalytic influence of water mentioned on page 317. This work seems to show that many reactions cannot take place at all in the absence of water. This objection has been answered by the assumption that such reactions are in fact proceeding, but infinitely slowly. The distinction, however, between a reaction which is proceeding infinitely slowly, and one which is not going at all, is clearly of theoretical interest only, and for purely practical purposes may be ignored. Or as P. Duhem has said: "It comes to the same thing experimentally whether we say that the velocity of a reaction is absolutely null, or that it is so small that there is no way of detecting it."

Again, there are cases where reactions give different products with different catalysts. Thus, alcohol in presence of nickel decomposes into acetaldehyde and hydrogen; whereas in contact with alumina, ethylene and water are formed. Similarly, carbon monoxide and hydrogen in presence of copper give formaldehyde; with chromic oxide, methyl alcohol; while in presence of nickel, methane and water result. Thus it appears that catalytic agents can not only start, accelerate or retard the speed of chemical reactions, but they can also in some cases direct or determine the course of a reaction.

The phenomena of catalysis are usually considered under two main headings, viz., homogeneous catalysis and heterogeneous catalysis.

Cases of homogeneous catalysis are those in which the catalyst is not separated from the reacting mixture by a surface. Thus, the commonest examples of this type are those of the catalysis of reactions in solution where the catalysts are also soluble. A typical example is the acceleration of the hydrolysis of ethyl acetate by the presence of a small quantity of a strong acid such as hydrochloric acid. The addition of the acid causes a very large increase in the rate of hydrolysis. As an example of homogeneous catalysis in the vapour phase, mention may be made of the fact that carbon monoxide and oxygen will not combine unless a trace of water vapour is present. (Cf. page 317.)

In heterogeneous catalysis, the catalyst is separated from the reacting mixture by boundary surfaces. Important examples are the manufacture of sulphur trioxide from sulphur dioxide and oxygen in the presence of platinum (see page 501); and the production of ammonia

by the combination of nitrogen and hydrogen in presence of iron and traces of molybdenum or (more usually) potassium and aluminium oxides (see page 429).

### § 10 Types of Catalyst

It is probable that almost all reactions are capable of being catalysed, and that almost all substances can act as catalysts for some reaction or other. There are, however, certain types of substances which exhibit catalytic power to a greater degree. These may be classified as follows:

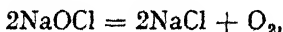
- (i) substances readily oxidizable and then easily converted back to their original condition;
- (ii) hydrogen ions;
- (iii) water;
- (iv) metals: in particular those of Group VIII of the Periodic Table.

The mechanism of these actions probably varies from case to case, but, in the main, it seems as though the action is to be ascribed to one or other of two main classes, viz.:

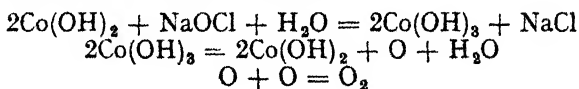
- (i) the formation of unstable intermediate compounds;
- (ii) the formation of a "condensed" layer of high concentration of reacting substances on the surface of the catalyst.

Considering now the types of catalyst mentioned above in the light of these ideas, we can attempt to find an explanation of the action in individual cases.

(i) Readily oxidizable compounds probably owe their effectiveness to the formation of intermediate compounds. An example of this type of catalysis is the decomposition of solutions of hypochlorites in the presence of cobalt oxide, whereby oxygen is evolved (see page 334). The equation for this reaction is simply (in the case of sodium hypochlorite):



but it is probable that the cobaltous hydroxide which is present in the mixture is oxidized to cobaltic hydroxide by the hypochlorite, and this being unstable readily loses oxygen, so reverting to the cobaltous condition, when the process is repeated:



Another example of this type of catalysis, and one of great industrial importance, is found in the manufacture of sulphuric acid by the chamber process in which the oxidation of the sulphur dioxide is catalysed by the presence of oxides of nitrogen (see page 496).

(ii) Hydrogen ion is a most efficient catalyst in many reactions. The acceleration of the hydrolysis of ethyl acetate by the addition of



hydrochloric acid mentioned above is an example of this, since all acids behave similarly and the common constituent of these is (on the Ionization Theory) the hydrogen ion. The precise mechanism of this action is not known with certainty, though Brønsted and his collaborators have met with a certain measure of success in the correlation of the catalytic effect of ions in general with modern views of valency. The subject is too advanced, however, for discussion here.

(iii) Water is apparently almost, if not quite, the universal catalyst. The majority of reactions appear to be retarded enormously, if not prevented altogether, by the intensive drying of the reacting substances. Very numerous examples of this effect are now known, chiefly through the work of H. B. Baker, and the whole subject is discussed in some detail in Chapter 20 (page 317) in the section on Water.

(iv) Metals. Whatever may be the explanation of the catalytic activity of the substances referred to in (i), (ii) and (iii) above (and it is quite possible that in many cases intermediate compounds are formed) the large group of catalysts comprised under the heading of metals can hardly be thought to act in this way. Certain metals, such as platinum, nickel and iron, are very effective catalysts, especially where hydrogen is concerned, and many of the examples of catalysis involving their use are of great technical importance.

The most probable explanation of this behaviour is thought to be connected with the fact that these metals have the power of absorbing or adsorbing\* large volumes of gases. It is believed that the gases contained in a reacting mixture are condensed on the surface of the metal in a layer one molecule thick; the local concentrations of the reacting substances being thus greatly increased and hence the rate of reaction.

That this is the *basis* of the effect seems highly probable, but that it is not the whole explanation seems equally certain. Thus, the acceleration of some reactions is too great to be accounted for in this way, although the fact that the greater the *surface* area of the catalyst, the greater the effect, shows that this is important.

Again, the fact that different catalysts can bring about the formation of different products from the same reacting substances seems very difficult to explain.

The observation that the occurrence of wall-reactions causes reactions of higher order than one to appear unimolecular (pseudo-unimolecular reactions), referred to in § 8, can now be understood. For, if the reaction is only taking place on the surface of the walls of the vessel or other catalyst, the active mass of the reacting substance is that in the layer adsorbed on the surface of the catalyst. When all the adsorbing area is covered, the rate of reaction will not be proportional to the pressure of the gas, and hence the true order of the reaction

\* An increase in the concentration or condensation of matter on a surface is called *adsorption*.

is obscured. Below a certain value of the pressure, of course, the rate of reaction will be such as to indicate truly the order of the reaction; for all the adsorbing surface will not be covered. But in general this condition is not observed.

Among important examples of catalysis by metals may be mentioned the following:

(i) combination of hydrogen and oxygen in presence of platinum (see page 291);

(ii) combination of sulphur dioxide and oxygen to form sulphur trioxide in presence of platinum (Contact process for sulphuric acid, page 501);

(iii) combination of nitrogen and hydrogen to form ammonia in presence of iron (Haber process, page 429);

(iv) oxidation of ammonia to nitric acid in presence of platinum (Ostwald process, page 448);

(v) the hardening of oils by hydrogenation in presence of finely divided nickel; used in the margarine and soap industries.

The last four are of great technical importance, being the basis of large industries, and the industrial applications of catalysis are constantly being increased. Several of these are referred to again in later chapters.

### Promoters

It has been found that in some cases of catalysis, the addition of yet another substance, which of itself has no catalytic activity, causes an increase in the effectiveness of a catalyst already present. The effect might be called "the catalysis of a catalyst." A case in point is the addition of various oxides to the iron used as catalyst in the Haber process for the synthesis of ammonia (see page 429). This effect is usually found in the case of solid catalysts, and the added substance is known as a **promoter**. The way in which promoters act is uncertain. It has been suggested that they prevent the main catalyst particles from coalescing, or crystallizing into larger aggregates, so maintaining a larger active surface. But, as with catalysis in general, it is quite likely that there are different types of promoter action each of which requires to be explained in a different way.

Catalysis in general must be regarded as a term which covers a group of phenomena of many and various kinds, having only in common the fact that the speed of a reaction has been changed by the presence of "foreign" substances. It is unlikely, therefore, that any single explanation can be found for so many diverse effects.

## CHAPTER 18

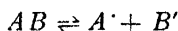
# THE APPLICATION OF THE LAW OF MASS ACTION TO ELECTROLYTES

The evidence is so unambiguous and convincing that ions and some molecules combine with more or less of the solvent, that it seems that it can now be accepted as a fact of science — H C JONES

### § 1 Ostwald's Dilution Law

ACCORDING to the Electrolytic Dissociation Theory of Arrhenius an electrolyte in solution at moderate dilutions consists of a system in equilibrium, viz., the undissociated substance and its ions. As such, its behaviour should be in conformity with the Law of Mass Action.

Thus suppose we have the substance  $AB$  undergoing ionization in solution, we have, according to Arrhenius, the equilibrium



and if we apply the Law of Mass Action it follows (using the same notation as previously) that

$$\frac{[A'] [B']}{[AB]} = k$$

The constant  $k$  is then known as the *ionization* or *dissociation constant*.

Suppose that we have 1 gram-molecule of electrolyte in  $v$  litres of solution, and that the degree of dissociation (cf. Chapter 15, § 6) is  $\alpha$ . Then, at equilibrium, the amount of non-ionized electrolyte will be  $(1 - \alpha)$  gram-molecules and of each of the ions  $\alpha$  gram-molecules. Substituting in the above expression we then have

$$\frac{\frac{\alpha}{v} \cdot \frac{\alpha}{v}}{\frac{1 - \alpha}{v}} = k$$

That is,

$$\frac{\alpha^2}{(1 - \alpha)v} = k$$

The application of the Law of Mass Action in this way was first suggested by Ostwald and the expression so deduced is the mathematical form of what is known as **Ostwald's Dilution Law**.

The experimental testing of this expression was at once undertaken, and a large number of organic acids was investigated from this point

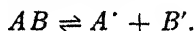
of view by Ostwald himself, while Bredig examined a number of bases. As a result, the law was found to hold excellently for *slightly ionized* (or *weak*) electrolytes, but to be very wide of the mark for *highly ionized* (or *strong*) electrolytes.

This failure of the Law of Mass Action in this form to apply to any but weak electrolytes has caused much attention to be directed to the revision of the Ionic Theory, since the consistent success of the Law of Mass Action in every other field in which it has been tested makes it very improbable that it is at fault. This matter has been referred to in Chapter 15, § 8, where an outline of the attempts to surmount the difficulty has been given.

## § 2 Solubility Product

Although the exact quantitative application of the Law of Mass Action to electrolytes in solution is somewhat limited in scope, we are able, nevertheless, to use the law in the elucidation of many of the phenomena connected with precipitation, and the behaviour of mixed electrolytes.

Let us consider first the state of affairs existing in a *saturated* solution of an electrolyte  $AB$  which ionizes thus:



The system "solid-saturated solution" is heterogeneous but, if we assume that the active mass of the undissociated solid in the liquid (i.e., solution) phase is constant, the Law of Mass Action is applicable and gives the expression

$$\frac{[A'] [B']}{[AB]} = k$$

where  $[AB]$  represents the active mass of the undissociated solid in solution. Now, in a solution, if by any means the concentration of either ion be increased, the equilibrium is disturbed and when, as in the case under discussion, the solution is already saturated, this means that the solution will tend to become over-saturated, and hence some solid will be precipitated. This is in agreement with experiment, for it is found that the solubility of a salt is usually diminished in the presence of another compound with a common ion, a phenomenon sometimes known as the *common ion effect*. Further, in a saturated solution, at a given temperature,  $[AB]$  being constant, the expression given above may be rewritten

$$\begin{aligned} [A'] [B'] &= K[AB] \\ &= K_s \end{aligned}$$

where  $K_s$  is a new constant which is called the **Solubility Product** of the substance. We see, too, that a condition for saturation of a solution is that the product of the concentrations of the ions should be equal to the solubility product.

Strictly speaking the solubility product relation applies only to saturated solutions of slightly soluble electrolytes but the same principles evidently hold in a qualitative kind of way in more concentrated solutions.

Familiar examples of this phenomenon are the precipitation of sodium or potassium chlorides from saturated solutions by passing hydrogen chloride through the solutions, or by adding a concentrated aqueous solution of the acid. The phenomenon is quite general. Barium chloride may be substituted for sodium chloride; again, concentrated nitric acid will precipitate barium nitrate from saturated aqueous solutions; a nearly saturated solution of silver bromate will give a precipitate of silver bromate, if either silver nitrate or sodium bromate be added to the solution; sodium chlorate added to a saturated solution of potassium chlorate will lead to the precipitation of the last-named salt.

It may be that these precipitations are not explicable solely by the application of the concept of the solubility product. The removal of some of the water by forming hydrated ions (e.g. hydroxonium ions from the hydrogen chloride, see page 269) may be an additional factor since this also increases the effective concentration of the other ions present.

### § 3 Application to Qualitative Analysis. Precipitation

These conclusions enable us to understand the reasons for many of the operations of ordinary qualitative analysis, in which identification and separation of the different substances present depends to a large extent on their solubility (or precipitation) relationships.

A substance is precipitated from solution when that solution tends to become supersaturated; or, in the light of the preceding section, when the product of the concentration of its ions tends to exceed the solubility product.

Now suppose we have a normal solution of silver nitrate and add to it an equal volume of a normal solution of hydrochloric acid. There will be an immediate formation of a precipitate of silver chloride. The reason for this is now clear. The silver nitrate and the hydrochloric acid are both highly ionized substances and so there will be, in their respective solutions, concentrations of silver ion and of chloride ion of something approximating to one gram-ion per litre. The mixed solutions would therefore contain about 0.5 gram-ion per litre of each. The product of these concentrations thus is

$$[\text{Ag}^+][\text{Cl}^-] = 0.25,$$

whereas the solubility product of silver chloride is only  $1.5 \times 10^{-10}$ . Hence the immediate and virtually complete precipitation of silver chloride.

The separation of the metals into groups in qualitative analysis depends upon the different solubilities of their sulphides in different

circumstances. Thus, one group comprises metals whose sulphides are precipitated in acid solution (e.g., copper and cadmium), whereas others (e.g., zinc and manganese) are only precipitated as sulphides in alkaline solution. The reason for this behaviour can be understood in the light of the foregoing.

In a saturated solution of hydrogen sulphide, there will be a certain concentration of sulphide ions and of hydrogen ions related according to the expression:

$$\frac{[H^+]^2[S'']}{[H_2S]} = k,$$

the actual concentrations of the ions being small since hydrogen sulphide is only feebly ionized in solution (cf. § 4 below). The addition of hydrochloric acid to this solution will cause a large increase in hydrogen ion concentration, since hydrochloric acid is highly ionized in solution. In order to maintain the equilibrium, therefore, the concentration of sulphide ions must be diminished, that is to say, the ionization of the hydrogen sulphide is driven back. In fact, the concentration of sulphide ions in a saturated solution of hydrogen sulphide is approximately  $10^{-8}$  gram-ion per litre in absence of hydrochloric acid; whereas in the presence of twice normal hydrochloric acid it is only  $10^{-20}$  gram-ion per litre.

Now suppose we have a solution containing soluble salts of copper, cadmium, and manganese, each of about "normal" concentration. The solubility products of the sulphides of these metals are approximately:

Copper sulphide . . . .	$1 \times 10^{-44}$
Cadmium sulphide . . . .	$1.4 \times 10^{-28}$
Manganese sulphide . . . .	$1.4 \times 10^{-15}$

The concentration of copper ion in a normal solution will be slightly less than 0.5 gram-ion per litre since the copper salt will not be completely dissociated at this concentration and the copper ion is divalent. The concentration of sulphide ion in presence of hydrochloric acid is, as we have seen, approximately  $10^{-20}$  gram-ion per litre. So that, if we add hydrochloric acid to the solution of the copper salt and then saturate the solution with hydrogen sulphide, we have

$$C_{Cu^{++}} \times C_{S^{--}} = 0.5 \times 10^{-20}$$

a number many times larger than the solubility product of copper sulphide, which is therefore precipitated.

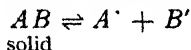
A similar value would result for the product of the concentrations of the metal ions and sulphides in the case of solutions of salts of the other metals named. In the case of cadmium sulphide the solubility product is exceeded and so it is precipitated; but the solubility product of the sulphide of manganese is not reached so that it is not precipitated.

It can be readily understood that, as indicated on page 484, the

division into groups of sulphides which are insoluble, or soluble, in acid solution is, to some extent, arbitrary since it depends upon the concentration of the acid (and hence of hydrogen ions) present.

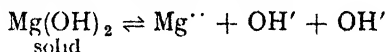
Similar considerations explain why the hydroxides of iron, chromium and aluminium are precipitated by the addition of a solution of ammonia to solutions of salts of these metals to which ammonium chloride solution has been added, whereas the hydroxides of manganese, cobalt, nickel, zinc, calcium, etc., are not precipitated.

The common-ion effect which is involved in the above explanations also applies in the reverse way in the solution of precipitates in some cases. For example, just as in the equilibrium,



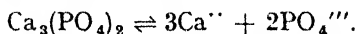
the addition of a solution of a substance giving the ions  $A'$  or  $B'$  will cause precipitation, the addition of any solution causing removal of either  $A'$  or  $B'$  will bring about solution of some of the solid  $AB$ .

As an example, we may take the case of a solution of a magnesium salt. The addition of ammonia solution will cause the precipitation of magnesium hydroxide. If now we add excess of a strong solution of ammonium chloride, the large increase in the concentration of ammonium ions which results (ammonium chloride being largely dissociated at moderate dilutions) drives back the dissociation of the ammonium hydroxide, and hence reduces the concentration of hydroxyl ions to a very small value. The equilibrium:

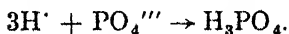


is thereby upset and some, if not all, the magnesium hydroxide will dissolve again.

The observation that insoluble salts of weak acids (cf. § 4) are often soluble\* in solutions of strong acids can be explained similarly. Thus calcium phosphate is very sparingly soluble in water but, on addition of dilute hydrochloric acid, a clear solution is obtained. Thus, it may be supposed that in the absence of acid the calcium phosphate gives rise to calcium ions and phosphate ions:



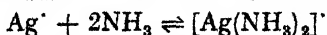
Phosphoric acid is a very weak acid (i.e., it furnishes very few ions in solution), consequently the addition of hydrochloric acid, which increases largely the concentration of hydrogen ions, will remove  $\text{PO}_4'''$  ions from the solution



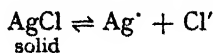
\* Objection is sometimes raised to the use of the word *soluble* to describe the behaviour of calcium phosphate with mineral acid and similar reactions in which the solution is the result of chemical action. Many prefer to restrict the terms *dissolve*, *soluble*, etc., to purely physical processes, but it is not always easy to draw the line between physical and chemical "solution."

This will upset the equilibrium between the solid calcium phosphate and its ions so that more will dissolve.

Another related phenomenon is the solution of precipitates by the addition of a soluble substance which can form a *complex ion* with ions derived from the precipitate. A familiar example is the solution of a silver chloride precipitate in aqueous ammonia. This is a consequence of the fact that silver ions will combine with ammonia to form a complex ion  $[\text{Ag}(\text{NH}_3)_2]^+$  and that the equilibrium



lies far over to the right-hand side; that is to say, at equilibrium there are very few silver ions ( $\text{Ag}^+$ ) left in the solution. A precipitate of silver chloride in contact with water maintains the equilibrium



and although, owing to its very low solubility product, the concentration of silver ions is low, it is yet much greater than that at equilibrium with argentammonium ion, so that addition of ammonia causes silver chloride to go into solution again.

A similar fact is made use of sometimes in separating copper from cadmium in qualitative analysis, by addition of excess of potassium cyanide solution. Complex ions are formed which are in equilibrium with only small concentrations of the simple metal ions; but whereas the complex ion formed from copper is in equilibrium with only a very small concentration of copper ions, that from cadmium requires a considerable concentration of cadmium ion for equilibrium. The result is that the concentration of copper ion is so low that on passing hydrogen sulphide into the solution, the even very small solubility product of copper sulphide is not exceeded and so no precipitation results. In the case of cadmium, however, the cadmium ion is present in sufficiently high concentration for the solubility product of cadmium sulphide to be exceeded and so it is precipitated.

#### § 4 Strengths of Acids and Bases

Many definitions of an acid have been given (see, for example, Chapter 21, § 9), but from the point of view of the Ionic Theory an acid is defined as a substance which when dissolved in water (or an ionizing solvent) furnishes hydrogen ions as the only positive ion. A base similarly, in terms of the Ionic Theory, is a substance which yields hydroxyl ions as the only negative ion, when dissolved in an ionizing solvent (usually water). The general and characteristic properties of acids are thus those of hydrogen ions, and those of bases are the properties of hydroxyl ions.

These conceptions give us a means of investigating the problem of the strengths of acids and bases. We say that sulphuric acid, for example, is a strong acid, and that acetic acid is a weak one, since the former will attack more substances (particularly metals) with greater vigour than the latter. But this criterion is vague, arbitrary and often misleading. As shown below, the Ionic Theory (in conjunction with the Law of Mass Action) furnishes us with a criterion applicable to a great many cases, and giving results in harmony with other methods.



The action of sulphuric acid on sodium chloride (page 538), which results in the formation of hydrochloric acid, seems to prove that sulphuric acid is stronger than hydrochloric acid; but when hydrochloric acid is added to a solution of silver sulphate, silver chloride is precipitated. The hydrochloric acid expels the sulphuric acid from its combination with silver:



and it seems as if hydrochloric acid is stronger than sulphuric acid. These two conclusions are contradictory and there must therefore be a fallacy in the reasoning. We have wrongly assumed that the two acids were competing for sodium and for silver under similar conditions. This is not the case. When hydrochloric and sulphuric acids compete for the sodium, the hydrochloric acid, being volatile, escapes from the system as fast as it is formed; while the non-volatile sulphuric acid alone remains behind. Again, when sulphuric and hydrochloric acids are competing for silver, the hydrochloric acid carries the silver away from the sulphuric acid as an insoluble precipitate of silver chloride.

To compare the relative strengths of the acids, and, *mutatis mutandis*, of the bases, it is necessary that the comparison be made under conditions where the reacting acids and the products of the reaction are in the same physical condition — say, all in solution. Thus, if an equivalent of sodium hydroxide be mixed in dilute solution with an equivalent of sulphuric acid and an equivalent of hydrochloric acid, the two acids can compete for the one base under the same conditions, and hence the stronger acid will be able to unite with more sodium than the weaker acid. In 1803, C. L. Berthollet pointed out that when a neutral salt is dissolved and an acid is added to the solution, the free acid enters into competition, with the combined acid, and they both act on the alkali base in the ratio of their respective concentrations as though no combination had existed. It cannot therefore be said that if all the conditions remain equal, one acid displaces another from the base with which it had been united, but the base is shared between the two acids. The proportion in which it is so shared depends upon the concentrations of the respective acids as well as their strengths in the sense in which that word is used in this section.

It is found experimentally that the same result is obtained when equivalent quantities of sodium hydroxide, sulphuric acid, and hydrochloric acid are mixed together, as when equivalent quantities of sodium sulphate and hydrochloric acid, or equivalent quantities of sodium chloride and sulphuric acid, are mixed, provided, of course, the whole of the system has been allowed to stand long enough for equilibrium.

The proportions of a base shared between two acids, or of an acid between two bases, cannot be determined by the ordinary methods of chemical analysis without disturbing the equilibrium of the mixture. The distribution of an acid between two bases, or of a base between two acids, must be determined by physical processes which do not interfere with the solution. In illustration, the equivalent heat of neutralization of sodium hydroxide by sulphuric acid is 15.69 Cals.; and by hydrochloric acid, 13.74 Cals. If, therefore, on mixing hydrochloric acid with sodium sulphate, all the sulphuric acid were displaced by the hydrochloric acid, the thermal effect resulting from the decomposition of the sodium sulphate, and the formation of the sodium chloride, would be  $13.74 - 15.69 = -1.95$  Cals. After making a small allowance for secondary reactions between sodium sulphate and sulphuric acid, J. Thomsen found that the thermal value of the reaction was  $-1.3$  Cals. Hence it follows that  $-1.3 \div -1.95$  or about two-thirds of the hydrochloric acid combines with about two-thirds of the base to form sodium chloride; and about one-third of the sulphuric acid combines with the other third of the base to form sodium sulphate. A similar result was obtained with a mixture of sodium chloride and sulphuric acid as with sodium sulphate and hydrochloric acid. Consequently, in the competition of sulphuric and hydrochloric acids for sodium under comparable conditions, the hydrochloric acid can hold twice as much of the base as the sulphuric acid, and consequently, hydrochloric acid is nearly twice as strong as sulphuric acid.

Similar results have been obtained by measuring the specific gravity, index of refraction, absorption of light, etc. The relative strengths of the different acids have also been determined by measuring the effects of the different acids on the speed of hydrolysis of cane sugar, methyl acetate, etc.

From the point of view of the Ionic Theory, *the strength of an acid is related to the extent to which it furnishes hydrogen ions in stated circumstances, that is, to the concentration of hydrogen ions in solution.* The concentration of hydrogen ions depends upon the degree of ionization of the different acids. Hence the relative strengths of the acids can presumably be expressed in terms of the electrical conductivity of equivalent solutions. The speed of a reaction dependent upon an acid is thus connected with the concentration of the  $H^+$  ions. In hydrochloric acid, a greater number of hydrogen ions are ready to react with the metal than in acetic acid, and consequently the available hydrogen in hydrochloric acid is more rapidly exhausted than with acetic acid, where but few ions are in a condition to react with the metal at any moment, and consequently the reaction progresses slowly for a long time.

Hence hydrochloric acid is a stronger acid than acetic. On the assumption that the order of strength of acids is the same as that of the conductivities at corresponding dilution, we find that hydrochloric and nitric acids are of approximately equal strength and are both stronger than sulphuric acid. This is indicated in the last column of Table XXIV, which table shows the order of strengths of acids as deduced by several independent methods.

TABLE XXIV.—RELATIVE STRENGTHS OF ACIDS

	Thomsen's Thermal Method	Specific Gravity Method	Ester Hydrolysis Method	Conductivity Method
Hydrochloric acid . . .	100	100	100	100
Nitric acid . . .	100	100	91.5	99.6
Hydrobromic acid . . .	89	97	—	100
Sulphuric acid . . .	49	68	54.7	65.1
Phosphoric acid . . .	13	—	—	7.3
Acetic acid . . .	3	1.25	0.35	0.4

Hydrochloric acid has been taken as the standard of reference in this table and its strength arbitrarily called 100. The figures for the other acids thus express their strengths as percentages of that of hydrochloric acid.

This table shows that the results obtained by the different methods, although not in exact quantitative agreement, are yet sufficiently close to show that the order of strengths is consistent and that the relative strengths of these acids are very close to the values derived from any of these criteria. The discrepancies between them may be due to differences in the conditions under which the different determinations were made.

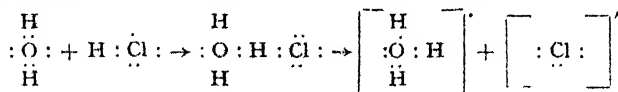
Similar results have been obtained from investigations on bases, from which it has been found that sodium hydroxide and potassium hydroxide are strong bases, whereas ammonium hydroxide is a weak base whose strength is not much more than 10 per cent of that of potassium hydroxide.

**Dissociation Constant.**—When Ostwald's Dilution Law (page 261) is applied to acids the constant,  $k$ , is known as the *Dissociation Constant of the acid*. Since this constant is then clearly a measure of the hydrogen ion concentration at a given dilution it is also a measure of the strength of the acid concerned (according to the definition given on page 268). Because Ostwald's dilution law is found to hold only for weak electrolytes it follows that dissociation constants can be found only for weak (and not for strong) acids. Similar considerations apply, of course, to weak alkalis.

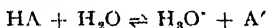
**The Hydroxonium Ion.**—The correlation, in the way just described, of the strength of an acid with the concentration of hydrogen ions in the solution requires some modification in the light of the modern view that the ion which is really concerned is the hydroxonium ion  $\text{H}_3\text{O}^+$  as discussed on page 228.

One of the difficulties of the simple ionic theory of acids is that, on modern theory, for a substance to ionize it must be an electrovalent compound, whereas many acids when quite pure do not conduct electricity and hence must be presumed to be covalent compounds. Consequently, the fact that they give conducting solutions requires some further explanation.

This explanation is furnished by the conception that the ion formed is not  $\text{H}^+$ , but  $\text{H}_3\text{O}^+$ . For water is capable of co-ordination (Chapter 11) and can act as a donor by virtue of the lone pairs of the oxygen atom. Considering the case of hydrogen chloride, assumed to be a covalent compound (when pure it is a non-conductor), the oxygen of a water molecule can co-ordinate on to the hydrogen chloride molecule giving a "molecule" which can now ionize, one of the ions being the  $\text{H}_3\text{O}^+$  ion. This may be illustrated by the scheme:



In general, therefore, the solution and ionization of a strong acid in water is to be represented by the equilibrium



and the phrase "hydrogen ion concentration" must be taken to refer to the  $\text{H}_3\text{O}^+$  or hydroxonium ion.

Lowry and Brønsted have used this reaction as a basis for different definitions of an acid and a base. They pointed out that the formation of the hydroxonium ion involves, in essence, the transfer of a proton from the molecule of acid to the molecule of water, and they therefore propose to define *an acid as any molecule, radical, or ion, which has a tendency to give up protons to a base*, a base, similarly, is then defined as *any molecule, radical or ion which has a tendency to accept protons from an acid*. According to Lowry and Brønsted's definition the molecule of anhydrous ammonia ( $\text{NH}_3$ ) is a base (which it is not in terms of the Ionic Theory) for it can react with hydrogen chloride, thus



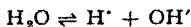
Similarly, the anion of a weak acid (such as the acetate ion) is, according to this theory, a strong base since it readily combines with protons forming the undisassociated acid.

## § 5 Salt Hydrolysis

It might be expected that solutions of salts made by the combination of equivalent quantities of acid and base would show a neutral reaction (cf. page 272), but, in many cases, this is found not to be true. Thus, for example, although solutions of sodium chloride are neutral, as would be expected, solutions of potassium cyanide are alkaline, while those of ferric chloride are acid.

The nature of this effect depends upon the relative strengths of the acid and base from which the salt is made. Thus, sodium chloride is the salt of a strong acid and a strong base and is therefore neutral. On the other hand, hydrocyanic acid is a very weak acid and hence its potassium salt (potassium hydroxide being a strong base) is alkaline in solution. Similarly, ferric hydroxide being a weak base, its salt with the strong acid hydrochloric acid is acid in aqueous solution.

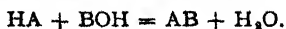
This behaviour of salts, known as salt hydrolysis, follows from the fact already noted in Chapter 15 (page 222) that water itself is very slightly dissociated into hydrogen and hydroxyl ions:



the product of the concentrations of these ions being approximately  $10^{-14}$  at ordinary temperatures, i.e.,

$$[H^+][OH^-] = 10^{-14}.$$

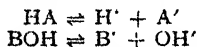
Now suppose that we have in solution a salt AB, being the salt resulting from the combination of the acid HA and the base BOH:



The salt in solution will be largely ionized



so that the solution will contain a high concentration of  $A'$  ions and  $B'$  ions and a slight concentration of  $H^+$  and  $OH^-$  ions from the ionization of the water. If the acid HA and the base BOH are both strong, nothing particular will happen, for the equilibria



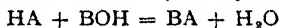
will be such that large concentrations of ions are in equilibrium with very small concentrations of acid or base. But suppose that the acid HA is a weak acid, that is to say, it only dissociates to a very slight extent in solution. The circumstances resulting from the solution of a salt of such an acid will then momentarily involve the coexistence in the solution of  $H^+$  ions along with a high concentration of  $A'$  ions, so the product of the two concentrations will largely exceed that required by the equilibrium relations of the acid, as defined by its dissociation constant, i.e.,

$$\frac{[H^+][A']}{[HA]} = \text{dissociation constant (small for a weak acid)}$$

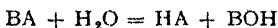
Accordingly hydrogen ions and  $A'$  ions will combine to form undissociated HA; the equilibrium between the  $H^+$  and the  $OH^-$  ions from the water is thereby upset, and more hydroxyl ions will be formed from the water to restore the equilibrium between the water and its ions. Hydroxyl ions will thus accumulate in the solution, which will therefore be alkaline.

A similar reasoning, *mutatis mutandis*, will show that the salt of a weak base with a strong acid will give an acid solution.

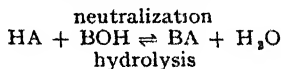
Neutralization (see page 340), which may be represented by the equation:



is, in one sense, the formation of a salt and water from an acid and a base. Hydrolysis is thus, in one sense, the formation of an acid and a base by the action of water on a salt:



and so is the reverse of neutralization. These facts may be conveniently summed up by combining these two equations into one:



## § 6 Indicators

The action of acids and alkalis in changing the colour of litmus solutions is one of the familiar facts of elementary chemistry. Substances such as litmus, which change colour in this way, are known as *indicators* and have been used to distinguish between these two groups of compounds at least since the time of Boyle.

Many natural colouring matters can be used for this purpose, the most important of which are *litmus*, obtained from certain lichens, and

**turmeric** which is obtained from the root of an Indian plant (the same as is used in making curry). Litmus is turned red by acids and blue by alkalis, while turmeric is yellow in acid, and brown in alkaline solution.

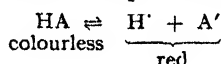
Many synthetic organic dyes are now used as indicators; those at present most used in volumetric analysis are **methyl orange**, either simple (red with acids, yellow with alkalis), or screened (see below), **methyl red** (red with acids, yellow with alkalis), **phenolphthalein** (colourless with acids, red with alkalis), **bromothymol blue** (yellow with acids, blue with alkalis), and **thymolphthalein** (colourless with acids, blue with alkalis).

Indicators are largely employed, not only for distinguishing between acids and alkalis, but also for determining the end point when titrating acids with alkalis either for the preparation of salts, or in the quantitative operations of acidimetry and alkalimetry in volumetric analysis.

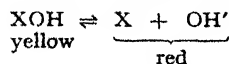
The colour change of some indicators in common use is not easy to detect, particularly in artificial light. Methyl orange is an example of this. A more easily noticeable end point can often be secured by using a mixture of the indicator with an indifferent dye. The use in this way of methyl orange mixed with another suitable dye such as indigo carmine or xylene cyanol FF has been found advantageous. These are examples of a **screened indicator**. The colour change in the latter case is from green  $\rightarrow$  grey  $\rightarrow$  magenta as the solution passes from the alkaline to the acid side.

#### Theory of Indicators

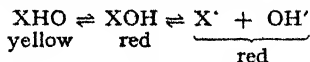
According to Ostwald's theory of indicators these substances are weak acids, or weak bases, whose colour is different according as they are in the ionized or non-ionized condition. Thus, according to Ostwald, the behaviour of phenolphthalein which is a weak acid is to be represented:



The addition of an acid will increase the concentration of hydrogen ions, so driving back the dissociation of the indicator which becomes colourless. Addition of an alkali reverses this process by removal of hydrogen ions. Similar considerations serve to explain the behaviour of an indicator, such as methyl orange, which is a weak base:



It is now generally believed that this is not the whole story, since marked change of colour in organic chemistry betokens a change of structure. This difficulty is met by the assumption, now well justified, that in addition to the equilibrium between undissociated indicator and its ions, there is another equilibrium between two forms of the indicator itself. This is represented in the following scheme:



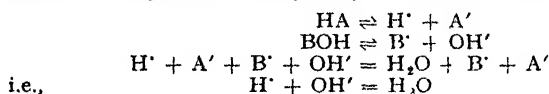
applicable to methyl orange. The same principles, however, still serve to explain the effect of acid or alkali in causing the change of colour of an indicator as the two equilibria are interrelated and interdependent.

### Choice of Indicator

Experiment has shown that an indicator changes colour within a small range of the hydrogen ion concentration of the solution which contains it and that this range is different for different indicators. A knowledge of the values of the hydrogen ion concentration during which the colour change takes place is thus important, as it determines the choice of indicator for a particular operation.

This choice depends also upon the way in which the hydrogen ion concentration changes with the relative proportions of acid and alkali, and we must now consider this in typical cases.

Neutralization as we have seen is, according to the Ionic Theory, primarily the combination of hydrogen and hydroxyl ions to form water



Strict neutrality is, therefore, achieved when the hydrogen and hydroxyl ion concentrations are equal (and equal accordingly to their values in pure water).

Now the value of the ionic product for water is constant in all aqueous solutions, at a given temperature, and approximately equal, as we have seen, to  $10^{-14}$  at  $18^\circ\text{C}.$ :

$$[\text{H}^+][\text{OH}'] = 10^{-14}$$

At the neutral point, the  $\text{H}^+$  and  $\text{OH}'$  concentrations are equal:

$$\text{i.e., } [\text{H}^+] = [\text{OH}'] = \sqrt{10^{-14}} = 10^{-7}$$

If the  $\text{H}^+$  concentration is greater than  $10^{-7}$  the solution is acid, if it is less than  $10^{-7}$  it is alkaline

This important quantity, the concentration of hydrogen ions, is sometimes represented by the number in the index of the value of the concentration and is then described as the *pH* value. Thus a neutral solution (concentration of  $\text{H}^+ = 10^{-7}$ ) has a *pH* = 7, and so on

It might be thought from this that the indicator required for any titration or neutralization was one which changes colour when the *pH* value of the solution is 7. But a little consideration will show that this is not always the case. In the preceding section we saw that many salts are hydrolysed in solution and that their solutions in consequence are not strictly neutral, but acid or alkaline according as the acid or base from which the salt was made was the stronger. Conversely, it follows that although chemically exactly equivalent quantities of an acid and a base have been mixed, the solution will only be neutral (i.e., have a *pH* value of 7) if acid and base were both equally strong. So that it follows that the choice of indicator for any particular titration is determined by the hydrogen ion concentration of the solution when chemically equivalent quantities of acid and base are present

The *pH* ranges at which some indicators mentioned above change colour are approximately as follows.

- \* litmus: 5.0 to 8.0
- bromothymol blue: 6.0 to 7.6
- methyl red: 4.2 to 6.3
- methyl orange: 3.1 to 4.4

\* Litmus is not now used in quantitative work since, being the extract of a natural product, it is liable to contain varying amounts of the colouring matter. It is useful in qualitative tests; for these litmus paper is better than the solution.

thymol blue: 8.0 to 9.6  
 phenolphthalein: 8.3 to 10.0  
 thymolphthalein: 8.3 to 10.5

From these figures we can derive the general rules indicated in Table XXV as to the choice of indicator for a particular titration:

TABLE XXV.—CHOICE OF INDICATORS

For the titration of	Use, as indicator
Strong base and strong acid	Methyl orange or bromothymol blue
Weak base and strong acid	Methyl orange or methyl red
Strong base and weak acid	Phenolphthalein, thymol blue or thymolphthalein
Weak base and weak acid	None satisfactory

The fact given in the last line of the table is easily explained when it is remembered that the salt of a weak base and a weak acid is almost completely hydrolysed in solution, and that as the acid and base are both weak, at no point during such a titration will the hydrogen ion concentration be far removed from that corresponding to neutrality (i.e.,  $10^{-7}$ ). Accordingly there is no sharp change in  $H^+$  ion concentration, so that no indicator will show when equivalent quantities of acid and base are present, in these circumstances. The titration of a weak acid by a weak base is consequently a process to be avoided.

The conclusions summarized in Table XXV are also supported by investigations into the way in which the hydrogen ion concentration of a solution changes with the relative amount of acid and base present in the neighbourhood of the equivalent point. The results of these investigations are summarized in the diagrams Figs. 18.1, 2, 3, 4, which show the changes in  $pH$  value with the relative amount of acid and base for some typical cases.

The curve of Fig. 18.1 shows this relation for the titration of a strong acid by a strong base (as, for example, hydrochloric acid and sodium hydroxide). The long straight portion indicates that, in the neighbourhood of the equivalent point, a very small excess of one or other reagent produces a very large change in the hydrogen ion concentration. Consequently, a suitable indicator will change colour very sharply, and as the straight portion of the curve extends over a wide range of  $pH$  values several indicators are available.

Fig. 18.2 shows the similar relation for the titration of a weak acid (such as acetic acid) with a strong base; and Fig. 18.3 that for the converse operation (strong acid, e.g.,  $HCl$ , and weak base, e.g.,  $NH_4OH$ ). In these the curve still has a considerable straight portion, but it is shorter than in Fig. 18.1. Also the middle of the straight part (corresponding to equivalence) is displaced from a  $pH$  value of 7, and so an indicator whose colour change occurs at a  $pH$  different (in the appropriate sense) from 7 is required.

Fig. 18.4 shows the curve for a weak acid and a weak base, and the absence of a straight portion shows that no indicator will mark the end point of this process.

**Buffer Solutions.**—It is sometimes necessary to have available a solution of known hydrogen ion concentration (or  $pH$ ), the  $pH$  of which does not differ appreciably on the addition of an acid (or base). Such solutions, which are known as **buffer solutions**, consist of a mixture of a weak acid (or weak base) with the salt of the acid with a strong base (or of the base with a strong acid).

A standard example is a solution containing acetic acid and sodium acetate. This has a  $pH$  value which is almost unchanged on dilution and which is only slightly altered by the addition of a strong acid.

Thus, the  $pH$  of a solution of deci-normal acetic acid, to which sufficient solid sodium acetate has been added to make it deci-normal in sodium acetate also, is 4.74 at  $25^\circ C$ . After addition of 10 ml. of normal hydrochloric acid to 1 litre of

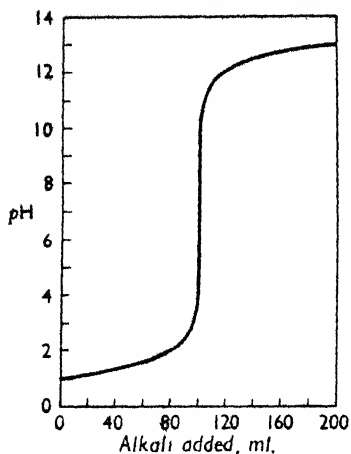


FIG. 18.1

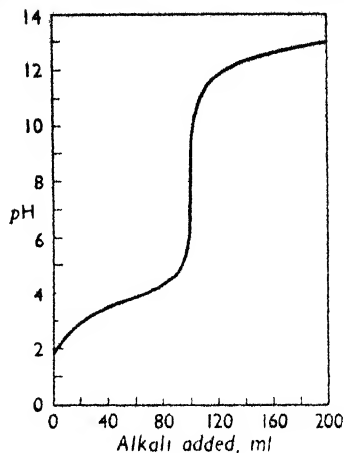


FIG. 18.2

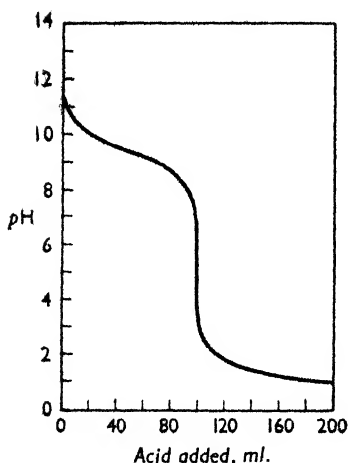


FIG. 18.3

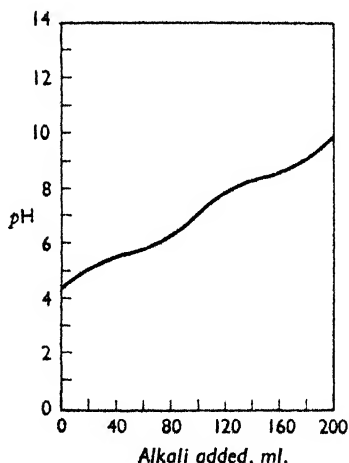
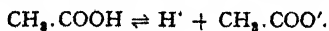


FIG. 18.4

this solution the pH of the mixture is 4.66. The similar addition of 10 ml of normal hydrochloric acid to 1 litre of water would change the pH from 7 to 2.

The reason for this behaviour can readily be understood in terms of the Ionic Theory. The acetic acid will furnish hydrogen ions and acetate ions



The sodium acetate, being a salt, may be regarded as almost completely ionized. On addition of hydrochloric acid (a strong acid) the hydrogen ions thus added combine with the acetate ions to form undissociated acetic acid and so are almost entirely removed. Consequently, the pH of the solution is virtually unchanged. Buffer solutions are thus said to possess *reserve acidity* (or *alkalinity*).



### § 7 Electrometric, or Potentiometric, Titration

The potential of an electrode, in contact with a solution of its ions, is proportional to the concentration of the ions with which it is in equilibrium. Consequently it is possible to use the measurement of such a potential in place of the usual "indicator" in volumetric analysis.

To carry out a titration the titrating liquid is run into the solution to be titrated in the usual way and the potential of the electrode is determined from time to time. For acid-alkali titrations a "hydrogen-electrode" (page 230) is used. A graph can then be drawn showing how the potential of the electrode changes with the volume of the solution added from the burette and a curve of the form shown in Fig. 18.5 results. The point of inflection on the curve then corresponds to the equivalence point. Titration carried out in this way is known as **electrometric** (or **potentiometric**) titration.

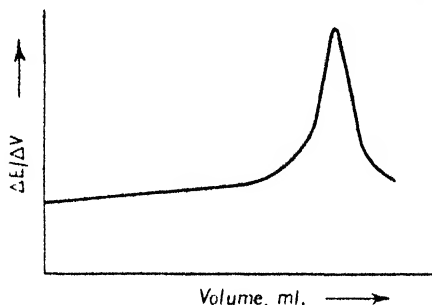


FIG 18.5 — Graph of potentiometric titration

In practice, the potential can be measured by means of the standard types of potentiometer but it is now possible to utilize one of several types of apparatus available, which employ thermionic valves, and which indicate the end point directly. For example, in one instrument the approach of the end point is indicated by temporary deflection of a galvanometer "spot" of increasing magnitude, while the end point is shown by a large and permanent deflection.

Potentiometric titration has the advantage of being applicable to any reaction for which a suitable electrode is available including some for which there is no suitable colour indicator. The results are very reliable (being less subjective than with colour indicators) and are susceptible of high accuracy. The method can also be employed for solutions which are too dilute for conventional volumetric analysis.

## CHAPTER 19

# THE COLLOIDAL STATE

I may be allowed to advert again to the radical distinction assumed to exist between colloids and crystalloids in their intimate molecular constitution. Every physical and chemical property is characteristically modified in each class.—T. GRAHAM.

### § 1 Graham's Experiments

It has already been mentioned (Chapter 13, page 178) that immediately between true solutions of solids in liquids and coarse suspensions, there exists a class of solid-liquid mixtures which are known as colloidal solutions. Again, in Chapter 14 (page 199) it was pointed out that soluble substances, like copper sulphate, can *diffuse* through a solution.

The phenomena of diffusion in general were extensively investigated by Graham, who, as we saw in Chapter 3 (page 32), was able to deduce, from the results of his experiments with gases, the law of gaseous diffusion known by his name, and which has been confirmed on the basis of the Kinetic Theory.

When later (in 1861) Graham turned his attention to diffusion in liquids, he found that there was often a very marked difference between the behaviour of different substances. This he noticed particularly when studying the rate of diffusion of salts through parchment paper, for he found that certain substances, such as glue or gelatine, diffuse through the parchment only very slowly: the membrane\* was almost entirely impervious to these substances, but substances like sodium chloride, or magnesium sulphate pass readily through such a membrane. Graham applied the term **colloids**—from the Greek *κόλλα* (*kolla*), glue—to those substances which diffuse but slowly through the parchment; and since crystalline salts are typical of those substances which diffuse rapidly, he called them **crystalloids**.

Subsequent experience has not upheld Graham's distinction between crystalloids and colloids as representing different kinds of substances; for many substances can exist in either condition according to circumstances. In consequence, it is now usual to consider these as *states*, rather than as *types* of matter, and accordingly we speak of substances whose behaviour is that which Graham associated with colloidal substances as being in the **colloidal state**. It is now known that, at any rate in a great many cases, the determining factor is the size of the particles concerned.

\* The membrane used in these experiments must be distinguished carefully from the semipermeable membranes used in osmotic pressure investigations, and which are impervious to dissolved solids of all kinds, allowing only the passage of solvent.

## § 2 Suspensoids and Emulsoids

Colloidal solutions fall into one or other of two definite classes, each of which exhibits certain definite characteristics. These two categories are known as **suspensoids** and **emulsoids** or as **lyophobic** and **lyophilic** colloids respectively.

Colloidal solutions consist of particles of the substance in the colloidal state (intermediate in size between the molecules of the solute in true solutions and the particles of coarse suspensions which settle out rapidly when allowed to stand) dispersed in a liquid medium, usually water. When the particles partake of the nature of solids, the solution is that of a **suspensoid**; if the dispersed particles are droplets of liquid an **emulsoid** is formed. Examples of suspensoids are arsenious sulphide, ferric hydroxide and gold; and of emulsoids are gelatine and albumin. In regard to viscosity and surface tension, colloidal solutions of suspensoids differ little if anything from water. Their stability is a consequence of their motion (the Brownian movement, see page 281) and particularly of the fact that the particles are electrically charged (see § 4 below). In the case of emulsoids, the viscosity is usually much greater than that of water, the surface tension lower, and the medium in which they are dispersed is taken up to a greater or less extent by the colloidal particles. The stability of these solutions, therefore, depends to a considerable extent upon the nature of the medium in which they are dispersed and not so greatly upon the electrical charge on the particles as in the case of suspensoids.

## § 3 Preparation of Colloidal Solutions

Colloidal solutions of suspensoids can be made either by breaking down more massive particles to "colloidal" size (dispersion methods) or by building up suitable particles from molecular size (condensation methods).

Since many colloidal solutions are unstable in presence of electrolytes (being precipitated or coagulated thereby - see § 4 below) it is necessary, in their preparation, to remove electrolytes as far as possible, also to use very pure materials and clean apparatus.

The principal methods available are:

- (i) Chemical precipitation, followed sometimes by *dialysis* (see below for explanation of this term).
- (ii) Electrical dispersion, e.g., Bredig's arc method.
- (iii) Mechanical dispersion.

Examples of the use of each of these methods will now be given.

### Chemical Precipitation

When a very sparingly soluble substance is precipitated from a very dilute solution, in circumstances such that the solution is practically

free from ions, a colloidal solution frequently results. Thus, for example, if a cold, dilute solution of arsenic trioxide in water is saturated with hydrogen sulphide, and then filtered to remove such coarse particles as have been formed, a colloidal solution of arsenic sulphide is obtained.



Similarly, if very dilute solutions of salts of silver or gold are reduced by certain substances (as, for example, phosphorus in ether, or formaldehyde) the metal is not precipitated but remains suspended in a colloidal solution, which is usually highly coloured, owing to scattering of the light by the minute particles of the metal.

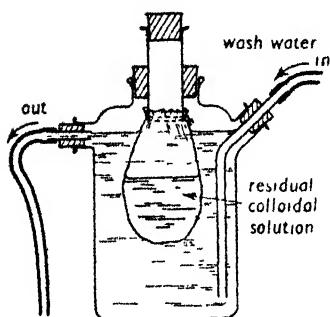


FIG. 19.1 —Dialyser

In some cases, owing to the presence of ions, chemical precipitation gives the colloidal substance in a more or less coagulated condition, from which a colloidal solution can be obtained by removing the electrolyte present. This is effected by the process known as **dialysis**, and which was proposed by Graham. It makes use of the fact already referred to that substances in the colloidal state do not readily pass through parchment membranes. The operation is carried out in a piece of apparatus called a dialyser, one form of which is illustrated in Fig. 19.1, and is similar to that used by Graham.

It consists of a parchment bag, containing the solution to be treated, immersed in a vessel through which a constant stream of water is kept running. Any non-colloidal substance (such as salt, or other electrolyte) will pass through the parchment and is carried away by the running water, while the colloidal substance remains.

More rapid dialysis is possible with membranes of collodion or cellophane. Collodion is convenient because its solution in a mixture of alcohol and ether, which is viscous, can be poured into a vessel of the shape and size required for the membrane and distributed over its inside surface, being then left to drain and dry. On immersion in water the collodion shrinks slightly and it is easily removed from the vessel. In this way membranes may be obtained of any suitable shape. A collodion membrane can also be prepared by deposition on a support such as cheese-cloth.

The use of dialysis is exemplified by the preparation of a colloidal solution of ferric hydroxide, sometimes called "dialysed iron." A few drops of ammonia are added to a solution of ferric chloride, and a reddish-brown precipitate of ferric hydroxide is formed. This redissolves in the unchanged ferric chloride. When the solution of ferric chloride is saturated with the ferric hydroxide, any further addition of

ammonia will give a permanent precipitate of ferric hydroxide. A few drops of hydrochloric acid are now added to dissolve the precipitated ferric hydroxide, and the solution is diluted with water so that it contains about 5 per cent of solid in solution. This solution is poured into the dialyser, the soluble ferric chloride and ammonium chloride pass into the outer vessel, and a dark red liquid remains in the inner vessel. This dark red liquid is the colloidal solution of ferric hydroxide.

A colloidal solution of silicic acid can be prepared similarly (see page 773).

### Bredig's Arc Method

When it is desired to obtain a colloidal solution of a metal by this method, an arc is struck beneath the surface of the liquid, using poles of the required metal and keeping the liquid cold by means of ice.

This method is particularly applicable to the production of dilute colloidal solutions of silver or platinum in water. It is believed that the metal is first torn off the poles in the form of vapour and that the sudden condensation by the water causes it to remain in the colloidal state.

### Mechanical Dispersion

Colloidal solutions can sometimes be made by fine grinding of the solid concerned. For example, indian ink is a rather coarse colloidal solution of "carbon" made by grinding lamp black with water and a little gum.

This principle has been extended recently in the use of the so-called "colloid mill." The substance which it is desired to get into colloidal solution is suspended as a coarse precipitate in water (or whatever liquid is to be used as the medium for the solution) and the whole is passed between two plates kept very close together and rotating in opposite directions at a speed of about 7000 revolutions per minute. By this process, only a proportion of the solid is ground sufficiently fine to form a stable colloidal solution, so that, in time, the large particles settle out; but a proportion is nevertheless reduced to particles of colloidal diameter.

Another dispersion method is that known as *peptization*. In this process certain substances become converted to the colloidal state when shaken with water containing very small quantities of ions. Examples are the formation of a colloidal solution of aluminium hydroxide, in presence of a trace of hydrochloric acid or of aluminium chloride, and of silver chloride by shaking the freshly precipitated substance with a very dilute solution of either potassium chloride or silver nitrate. Peptization will be seen to be the reverse of the coagulation of colloids by electrolytes discussed on page 282.

#### § 4 Properties of Colloidal Solutions

Colloidal solutions exhibit certain properties which are different in many respects from those of true solutions.

For example, colloidal solutions are not homogeneous, for a beam of light passed through such a solution is marked by a visibly luminous track, whereas a similar beam passing through water, or a true solution, is not as a rule visible in this way. This phenomenon is known as the Tyndall effect. Furthermore the light coming from this track is polarized, so that it is evident that there are present in the system particles which are sufficiently large to cause the scattering of light, although they are too small to be seen directly, even with the aid of a powerful microscope. The ability of the particles of a colloidal solution to scatter light can be applied, however, to the problem of determining both their number and their size, as is described in § 5 below.

A remarkable fact about colloidal solutions is that their particles are electrically charged; not that, as in the case of solutions of electrolytes, there are in a given solution equal numbers of particles of each electrical sign, but all the particles in a given solution are charged in the same sense. Also in some colloidal solutions the particles are always charged positively (for example, colloidal solutions of ferric hydroxide), whereas in others they are negatively charged (arsenic sulphide, for example). The existence of these charges is shown by the fact that if two electrodes, connected to a source of potential difference, are placed in a colloidal solution, the particles are found to move slowly towards one pole or the other, and by observing in which direction they move, the nature of the charge can be determined.

This movement in an electric field is known as **electrophoresis**. If an electric field is applied to a colloidal solution in such a way that the colloid particles are held stationary the dispersing medium will move. This effect is known as **electro-osmosis**.

It is the existence of the charge which, to a large extent, keeps the particles of a colloidal solution dispersed through the medium with which they form a colloidal solution. For since all the particles in a given solution carry the same charge, they are prevented by the natural repulsion between like charges from coalescing and so forming larger particles which would "settle-out." Granted that the particles are of sufficiently small size, and that they are prevented from coalescing, they will be kept dispersed through the medium by the molecular motion of the medium—the phenomenon known as the **Brownian Movement** (see below).

As a consequence of the fact that the particles of a colloidal solution are prevented from coalescing by the electrical charges which they carry, it follows that any disturbance of the system which tends to neutralize these charges will cause coalescence, and hence precipitation. This accounts for the fact that addition of electrolytes to colloidal solutions frequently causes precipitation; for the electrolyte furnishes

ions of both signs, one or other kind of which, being opposite in sign to the charge on the colloid particles, will discharge them and hence cause precipitation. It is also in accord with this observation that *the efficiency of an ion as a coagulating agent is roughly proportional to its valency*, that is, to the number of charges it carries. This is known as the *Hardy-Schulze Law* and is illustrated by the following figures which give the concentration of typical electrolytes having monovalent, divalent and trivalent cations required to precipitate arsenious sulphide (Table XXVI).

TABLE XXVI.—PRECIPITATION OF ARSENIOS SULPHIDE

Electrolyte	Concentration required (in gm.-mols. per litre $\times 10^{-3}$ )
NaCl	51.0
KCl	50.0
MgCl <sub>2</sub>	0.72
BaCl <sub>2</sub>	0.67
AlCl <sub>3</sub>	0.093

It is to be noted that, as the particles in a colloidal solution of arsenious sulphide are negatively charged, it is the *cation* which is effective in causing coagulation and precipitation. In the case of a positively charged colloid, such as ferric hydroxide, the efficiency of an electrolyte as precipitant depends upon the valency of the *anion*.

A further consequence of the differing sign of the charge on different colloidal particles is the fact that two colloidal solutions whose particles are oppositely charged will, when mixed, cause mutual precipitation. This is well illustrated by the action which takes place if suitable quantities of colloidal solutions of ferric hydroxide and arsenious sulphide are mixed. Both these solutions are coloured, but on allowing the mixture to stand the supernatant liquid becomes quite colourless if the proportions of the two solutions are correctly adjusted.

### The Brownian Movement

If very fine particles of an insoluble solid are suspended in a liquid they are found, on examination, to be in a state of motion which is quite continuous. This phenomenon is known as the **Brownian Movement**, after R. Brown, the botanist, who first observed it in 1827. It can be observed with particles of microscopic size, such as those of gamboge or lycopodium, and the smaller the size of the particles, the brisker the motion becomes. The Kinetic Theory of molecular motion seems to furnish the only admissible explanation of the phenomenon. According to this theory, the perpetual movements of the molecules of the liquid result in these molecules continually striking the suspended particles, thus driving them irregularly to and fro in the liquid. Since colloidal particles are much too small, as a rule,

to be seen directly under the microscope (see § 5), their motion, caused by the Brownian movement, will be vigorous and hence they show no tendency to settle out so long as they are prevented from coalescing into larger aggregates.

It is interesting to note that, using the assumptions of the Kinetic Theory, Einstein was able to calculate a relation between the motion of a particle undergoing the Brownian movement and the Avogadro Number (the number of molecules in a gram-molecule—page 85). This relation was used in the experiments of Perrin, and gave a value for  $N$  in good agreement with that obtained by a number of very different methods.

### Gels

Some concentrated colloidal solutions will often set to a jelly when cooled, and pass back into a solution again on warming. These are often, though not invariably, lyophilic colloids or emulsoids. Familiar examples are afforded by a gelatine solution or a soap solution, and the process of forming a jelly and re-liquefaction by alternate cooling and warming can be repeated an indefinite number of times. A jelly of this kind is found to have a heterogeneous structure, often of a honey-comb type, the cells being occupied by viscous liquid, and is known as a **Gel**.

Gels are also obtainable, at times, by coagulation. Thus, for example, if a colloidal solution of ferric hydroxide, prepared as described on page 278, be allowed to stand for some weeks in a glass vessel, a gelatinous solid is precipitated. Similar gels are obtained from silicic acid, and aluminium hydroxide, and like all gels they retain water very tenaciously, but when dried by the action of heat often exhibit the power of absorbing large quantities of water again. Some gels, such as silica-gel, differ from that of gelatine, for example, in that they do not liquefy again on warming, but otherwise the resemblance between the two types is close.

### Colloidal Electrolytes

Soap is an example of a colloidal electrolyte which is a salt, or acid, or base of which one ion does not form a true solution with water. When soap "dissolves" in water the sodium ions go into solution in the usual way and the solution becomes positively charged in consequence. The resulting electric field attracts the insoluble stearate ions into colloidal solution. These colloidal ionic particles are known as *ionic micelles*.

### Applications of Colloids

Colloids find many applications in industrial processes. Large quantities of silica-gel are manufactured for use as absorbents for gases, for which it is found to be as effective in many cases as charcoal.



Its ability to absorb large quantities of water has been made use of, for example, for the purpose of drying the blast used in the smelting of iron (see page 904). It also possesses the power of absorbing many substances from solution and has been applied to the removal of sulphur compounds from petroleum. It is almost certain also that dyeing is a colloidal process; certainly most dyes form colloidal solutions. Plastic clay becomes an easily pourable "slip" in the presence of a small percentage of alkali, a principle which is extensively used in the shaping of clay wares by casting. This is a very beautiful process and gives excellent results. The treatment of sewage is also a colloidal problem since a large proportion of the impurities are present in colloidal solution. The use of alum in precipitating sewage is explained by the efficiency of cations of high valency in bringing about the coagulation of negatively charged colloids. Other industrial processes involving colloids are the manufacture of paints and tanning; while they are intimately concerned in such diverse matters as the study of the soil, biological processes in general, and the formation of deltas at the mouths of rivers, but the discussion of these topics is outside the scope of the present work.

### § 5 The Size of Colloidal Particles and its Measurement

It has been noted above that the particles of a colloidal solution are too small to be seen directly, even with a powerful microscope. But the scattering of light which they are capable of causing, and which makes the track of a beam of light passing through the solution visible (a phenomenon known as the Tyndall effect), can be made use of in order to detect their presence, and hence to count them.

The way in which this is done is by means of the **ultramicroscope**, a device due to Zsigmondy. An intense beam of light—arc light, or better, a beam of bright sunlight—is focused into the liquid under examination, so that the light enters the liquid at right angles to the direction in which it is viewed under the microscope. This is illustrated, diagrammatically, by Fig. 19.2.

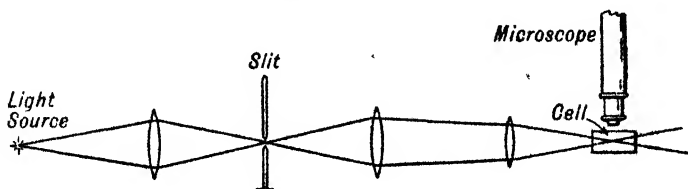


FIG. 19.2.—Ultramicroscope (diagrammatic)

While the opalescence of the Tyndall effect merely shows that a solution contains a number of distinct individual particles in suspension, the ultramicroscope enables the *individual* particles to be detected. The ultramicroscopic particles appear as glittering discs of light with a dim or dark background.

By means of the ultramicroscope, it is possible to count the particles in a minute, but known, quantity of a colloidal solution. If then the total weight of the particles present in a larger (but also known) volume of the solution is determined, it is possible to calculate their average size.

Other methods of determining the size of colloid particles are based upon the rate at which the particles settle (if they are large enough to do so); ultrafiltration; and the colour of the solution.

The first of these methods is only applicable to fairly large particles, as otherwise settlement is not sufficiently fast, even if it takes place at all. The calculation involves the use of an expression known as Stokes's Law, which gives a relation between the rate of settlement under gravity and the radius of the particle, the viscosity and density of the medium and the density of the particle being known.

Membranes can be prepared of different degrees of porosity so that colloid particles of different sizes may be separated by passing the solution containing them through such a membrane. Such membranes are known as **ultrafilters**, and can be prepared by impregnating filter paper with gelatine hardened with formaldehyde, or with collodion. By using solutions of different concentration, membranes of different porosity can be obtained and can be used to estimate the size of the particles of a given colloidal solution.

The relation between the size of colloid particles and the colour of their solutions depends upon the effect of small particles in causing the scattering of light, as mentioned above in connection with the Tyndall effect and the ultramicroscope. The scattering effect is greater for short waves than for long, and is also more marked the smaller the particles. On the assumption that these are spherical in shape, it is possible to calculate the size of particle necessary to give a certain (observed) colour. This has been tried experimentally and found to give results in satisfactory agreement with those of other methods.

## CHAPTER 20

# HYDROGEN AND WATER

Inflammable air is undoubtedly charged with abundance of the principle of inflammability.—T. BERGMAN (1779).

Water is absolutely indispensable to both animal and vegetable life; it is the cause of many of the most striking phenomena in nature; and it is employed for countless purposes by man.—P. F. FRANKLAND.

### § 1 History and Occurrence

#### History

It has been known for a very long time that an air or gas is produced when iron is dissolved in dilute sulphuric acid. T. B. Paracelsus, in the sixteenth century, described the action somewhat quaintly. He said that when the acid acts on iron "an air arises which bursts forth like the wind." J. B. van Helmont (*ca.* 1609) described this gas as a peculiar variety of air which was combustible and a non-supporter of combustion, but his ideas were somewhat hazy, for he confused hydrogen with other gases, like methane and carbon dioxide. Priestley, and writers generally up to about 1783, used "*inflammable air*" as a general term to include this gas, as well as the hydrocarbons, hydrogen sulphide, carbon monoxide, and other combustible gases. H. Cavendish (1766) showed that the inflammable air produced by the action of dilute sulphuric or hydrochloric acid on metals like iron, zinc, and tin was a distinct and definite substance, and A. L. Lavoisier (1783) called the gas "hydrogen."

#### Occurrence

The element hydrogen occurs free in nature in comparatively small quantities. The atmosphere is said to contain traces of hydrogen to the extent of one part per million or less. Hydrogen is also present in volcanic gases, in the gases from the Stassfurt salt beds and in some meteorites. The presence of hydrogen in natural gas from the oil fields has been denied, although many published analyses of these gases include "hydrogen." The sun's chromosphere shows what appear to be stupendous flames of incandescent hydrogen, in some cases towering over 300,000 miles (M. Fényi, 1892) into space, and 100,000 miles in width (C. A. Young, 1872)—thousands of times larger than the earth on which we live. Spectroscopic observations also show that hydrogen is present in nebulae and certain stars.

Combined hydrogen is common. Water contains one-ninth of its weight of hydrogen. Hydrogen, together with oxygen, is one of the

chief constituents of animal and vegetable tissue. Hydrogen also is present in nearly all organic compounds, and in many gases—methane, the hydrocarbons, hydrogen sulphide, etc.

## § 2 Production of Hydrogen

The methods available for the formation or preparation of hydrogen fall into three main groups:

- (i) The electrolysis of aqueous solutions;
- (ii) the displacement of hydrogen from its compounds by other elements;
- (iii) decomposition by heat of compounds containing hydrogen.

### Electrolysis

Pure water is ionized to such a very slight degree (see page 222) that it is almost a non-conductor and hence cannot be electrolysed. But the electrolysis of aqueous solutions of electrolytes which yield hydrogen at the cathode is often a convenient means of obtaining the element. Solutions of acids, bases or salts can be used according to the circumstances.

When such solutions are electrolysed, the positively charged ion will move to the cathode, and there be discharged and liberated. In solutions of acids the cation is a hydrogen ion, which, on reaching the cathode, is discharged and liberated as hydrogen gas. In solutions of bases or salts cations are metal ions and hydrogen ions from the water. If the metal be higher in the electrochemical series than hydrogen, the latter will be evolved at the cathode; if (cf. page 230) less electropositive than hydrogen, the metal will be deposited as such on the electrode. Consequently hydrogen can be obtained by the electrolysis of solutions of acids and of compounds of metals more electropositive than hydrogen.

### Displacement of Hydrogen

Hydrogen may be displaced by suitable means, either from water itself, or from solutions of acids and alkalis.

#### *Displacement from Water*

The more active metals, such as sodium, potassium, and calcium, will displace hydrogen from cold water; others, such as iron, zinc, and magnesium, will, when heated, decompose steam. The liberation from steam can also be brought about by the action of white-hot carbon, which produces a mixture of equal volumes of carbon monoxide and hydrogen, known commercially as water gas (see page 400). The hydrogen can be separated from the mixture by methods such as are described below.

*Displacement from Acids*

Acids are substances which contain hydrogen replaceable by a metal (see page 341). Many metals can replace this hydrogen directly, though, in the case of weak acids (cf. page 268), the action is only very slow. Also those metals which are below hydrogen in the electrochemical series (Table XIX, page 231) will not displace hydrogen directly, and acids which are also oxidizing agents, as, for example, nitric acid, enter into secondary reactions which often result in the hydrogen being oxidized to water (cf. Chapter 23, page 451). The action of diluted solutions of the common mineral acids, hydrochloric acid and sulphuric acid upon zinc, iron or tin, furnishes a convenient method for the preparation of hydrogen in the laboratory.

*Displacement from Alkalis*

A number of elements will react with concentrated solutions of alkalis, such as sodium hydroxide, with the liberation of hydrogen. Such are aluminium, tin and silicon, all of which displace hydrogen from a hot concentrated solution of caustic soda. The action may be represented in the case of aluminium by the equation:

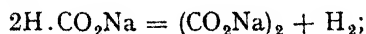


from which it is seen that in the other product besides hydrogen, viz., sodium aluminate, the aluminium is found in the electronegative (or acidic) radical, whereas when it is dissolved in hydrochloric acid it is the electropositive radical in the product (aluminium chloride).

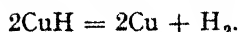
Zinc is usually said to react similarly with aqueous alkalis but it does so only with difficulty, if at all.

**Decomposition of Hydrogen Compounds by Heat**

Hydrogen results from the action of heat on substances such as sodium formate, which is thereby converted into sodium oxalate with evolution of hydrogen



and on certain hydrides such as that of copper,



These methods, however, are of theoretical interest only.

**§ 3 Preparation and Manufacture of Hydrogen***1. Preparation of Hydrogen in the Laboratory*

When required in any quantity in the laboratory hydrogen is now usually obtained from a cylinder of the gas; such cylinders are readily available commercially.

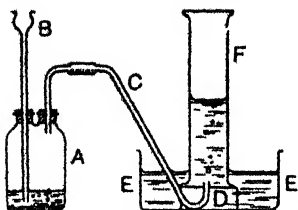


FIG. 20.1.—The Preparation of Hydrogen

On a small scale hydrogen is prepared by the action of dilute hydrochloric acid or sulphuric acid on granulated zinc using an apparatus similar to that shown in Fig. 20.1.

This apparatus consists of a two-necked Woulfe's bottle,\* *A*, fitted with a thistle funnel, *B*, extending nearly to the bottom of the bottle and with a delivery tube, *C*, as shown in the diagram.

The delivery tube dips under the **beehive shelf**, *D*, placed in a vessel of water, *E*. The vessels *D* and *E* form what is known as a **pneumatic trough**.†

Water is poured through the thistle funnel sufficient to cover the zinc, and concentrated sulphuric acid is then added, a little at a time until the gas begins to come off vigorously. It is important to make sure that all the air has been expelled before the hydrogen is collected in the **gas jars**, *F*. A test-tube full of the gas is collected and a light is applied to the mouth of the test-tube. If the gas detonates, the trial must be repeated until the gas burns quietly.

The reaction which is taking place may be represented by the equation:



If very pure zinc is used in this process the reaction may be very slow, but it can then be accelerated by the addition of a little copper sulphate solution. Iron filings or turnings can be substituted for zinc, but the gas is then very much more impure and has an unpleasant smell owing to the presence of hydrocarbons (i.e., compounds of carbon and hydrogen) formed by the action of the acid on iron carbides in the iron.

A more convenient way of obtaining hydrogen in the laboratory uses **Kipp's apparatus**, which is illustrated in Fig. 20.2. Pieces of zinc rod are placed in the middle bulb, *B*, and dilute sulphuric acid (1 volume of the concentrated acid to 8 volumes of water) or hydrochloric acid poured into the upper bulb, *A*, and so to the lowest vessel, *C*. On opening the tap *T* the acid rises into the bulb *B*,

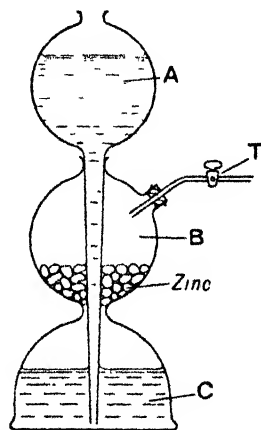


FIG. 20.2.—Kipp's Apparatus

\* The tubulated bottles for washing gases appear to have been first described by Peter Woulfe in 1784, hence the term **Woulfe's bottles**, not "Woulf's bottles."

† The discovery of the water pneumatic trough is often attributed to Stephen Hales, about 1730; J. Priestley afterwards used mercury in place of water, and this enabled him to manipulate gases soluble in water.

where it reacts with the zinc, generating hydrogen. When the tap is closed the evolution of gas continues for a time and the pressure so developed forces the acid into the upper bulb *A*, and so away from the zinc, thereby bringing the reaction to an end until the tap *T* is opened again.

For very accurate work, such as that involved in the determination of the combining ratio of hydrogen and oxygen (cf. Chapter 7, page 109), very pure hydrogen is required. Various methods have been employed for this purpose, but the most usual now is the electrolysis of a warm solution of recrystallized baryta contained in a hard glass tube, using nickel electrodes. This gives a relatively pure gas, but the last traces of impurity are removed by passing it over a hot platinum gauze where any trace of oxygen present is burned to water, then through tubes of caustic potash and phosphorus pentoxide to dry it; after which it is passed into an exhausted bulb containing warm metallic palladium foil which possesses the property of absorbing 800 times its volume of hydrogen. (Cf. Fig. 20.3.) Under these conditions only hydrogen is absorbed and so, by re-evacuating the bulb after cooling, all traces of gaseous impurities can be removed. On heating the palladium foil to a dull red heat, pure hydrogen is evolved.

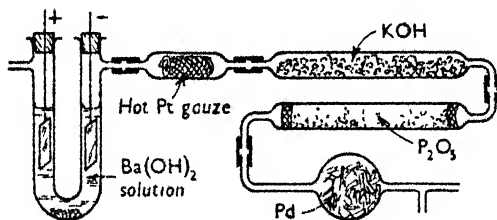


Fig. 20.3 — Preparation of Pure Hydrogen

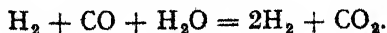
## 2. Manufacture of Hydrogen Industrially

The uses of hydrogen in industry are increasing in number and variety, as mentioned in § 8 below, and so the production of hydrogen cheaply, and in quantity, is a matter of prime importance. The most important industrial methods for making hydrogen are by extraction from water gas and by electrolysis.

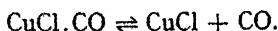
Water gas is the name given to that mixture of hydrogen and carbon monoxide and a trace of carbon dioxide which is formed when steam is passed over white-hot coke (see page 400).



In the **Bosch process** the water gas is mixed with more steam and passed over a catalyst, consisting of ferric oxide mixed with a trace of chromic oxide heated to  $450^\circ\text{--}500^\circ$ . The steam and water gas react with the production of hydrogen and carbon dioxide:



The carbon dioxide is removed by washing the gas with water under a pressure of about 25 atmospheres. Traces of unchanged carbon monoxide are then removed by means of an ammoniacal solution of cuprous chloride at 200 atmospheres pressure. The carbonyl salt formed is decomposed by heat when the solution has become saturated



Hydrogen is manufactured by the electrolysis of a 20 per cent solution of sodium hydroxide in cells fitted with nickel or iron electrodes; oxygen is obtained at the same time.

Very large quantities of hydrogen result as a by-product of the manufacture of caustic soda by the electrolysis of sodium chloride solutions (see page 532).

#### § 4 Properties of Hydrogen

Hydrogen is a colourless gas without taste or smell, though as ordinarily prepared it may contain traces of impurities (hydrocarbons or arsine) which give it an unpleasant smell. The gas is combustible, for on plunging a lighted taper into a jar of the gas held mouth downwards, it burns with a scarcely visible blue flame at the mouth of the jar, but the taper is extinguished, thus showing that hydrogen is a non-supporter of combustion. Its specific gravity is very low in comparison with air, being only 0.069, and its normal density is 0.089882 gm. per litre.

Hydrogen is not very soluble in water—100 volumes of water at 0° absorb 2.14 volumes of gas, and at 20°, 1.82 volumes of gas. Hydrogen was once used as the standard for atomic weights because it is the lightest element known, but this was later abandoned in favour of the oxygen standard, for the reasons explained in Chapter 7, page 103.

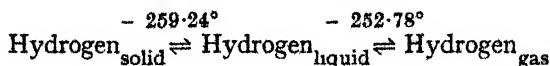
Hydrogen is not poisonous, but animals placed in hydrogen are suffocated for the want of oxygen. When hydrogen is inhaled, the voice becomes shrill—approaching falsetto. The pitch of organ pipes and other wind instruments is raised if a blast of hydrogen be used in place of air. This is in agreement with the deduction that the frequency of a note varies inversely as the square root of the density of the gas.

The critical temperature of hydrogen (page 43) is very low, being, in fact,  $-239.9^\circ$ , so that it is much more difficult to liquefy than air, or most other gases. Furthermore, when hydrogen under pressure is allowed to expand through a small orifice, unlike most other gases which are cooled by this process, hydrogen gets hotter, unless the temperature of the gas, before expansion, is below  $-205^\circ \text{C}$ . Below this temperature, hydrogen behaves like air and is cooled when allowed to expand suddenly through an orifice.

Just below the critical temperature, a pressure of about 20 atmospheres will liquefy the gas. The liquid is clear and colourless, resembling water, but its density is 0.07 grams per ml. at its boiling point

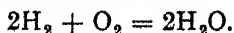


which is  $-252.78^{\circ}$  at 1 atm. Hydrogen solidifies when the liquid is evaporated in a partial vacuum. The white solid is crystalline, melts at  $-259.24^{\circ}$ , and has a specific gravity 0.08. The data concerning the change of state of hydrogen can be symbolized:



The spectrum of hydrogen, usually obtained by an electrical discharge in a vacuum tube, is simpler than that of most elements. As long ago as 1885, Balmer showed that a series of prominent lines which it contained (usually known as the Balmer series) could be expressed by the formula  $R \left( \frac{1}{2^2} - \frac{1}{n^2} \right)$ , where  $R$  is a constant, and  $n$  is a small whole number. In addition to the Balmer series, the spectrum is interspersed with fine lines, and, as mentioned in Chapter 11 (page 148), Bohr, on the basis of his theory of the structure and behaviour of the atom, was able to account for this expression, and also, by making allowance on relativity principles for the variation in the mass of the electrons with their velocity, was able to explain the fine-line structure to a great extent.

Hydrogen, as has been mentioned, is a combustible gas; the product of the burning of hydrogen in air is water:



The recognition of this fact constituted one of the landmarks in the progress of chemistry and is more fully discussed below. If instead of allowing the hydrogen to burn at a jet it is mixed with air or oxygen, the mixture on ignition explodes with great violence. The combustion of the whole mass is almost instantaneous. The explosion is so violent that N. Lemery believed thunder to be due to the "fulminations of hydrogen."

Hydrogen and oxygen, so far as can be detected, do not react at room temperature in the absence of catalysts; though some maintain that the gases do react, though very, very slowly (cf. page 257). Reaction under normal conditions is perceptible at  $180^{\circ}$  and explosive at  $550^{\circ}$ . In the presence of certain catalysts, such as palladium black, or platinum black, combination will take place at room temperature, and the heat evolved is sufficient to cause the gases to ignite.

Although the combustibility of hydrogen is one of its most characteristic properties, perfectly dry hydrogen ignites with difficulty; if at all, when mixed with perfectly dry oxygen, even at  $900^{\circ}$ . Similarly many other combustible substances, if perfectly dried, do not burn when moisture is rigorously excluded. This phenomenon is discussed more fully on page 317.

## Hydrides

Many elements form hydrides and these substances fall into three categories, viz., covalent hydrides, which are usually gaseous at ordinary temperatures (e.g., hydrogen chloride, hydrogen sulphide), salt-like hydrides, which are solids (e.g., sodium hydride), and alloy hydrides

(e.g., palladium hydride), a term held to include any substance formed when a metal absorbs or occludes hydrogen and where there is no evidence of the formation of a covalent or salt-like hydride. Alloy hydrides are probably not true chemical compounds at all and their nature is still a matter for investigation and discussion.

The various covalent hydrides known are discussed under the heading of the elements concerned. Saline hydrides are formed by the alkali metals and calcium, strontium and barium among the alkaline earths. They are powerful reducing agents; lithium aluminium hydride (page 747) is an important reducing agent in organic chemistry.

It is interesting to note that in the case of the metallic hydrides, when electrolysis is possible (e.g., fused lithium hydride) the hydrogen is liberated at the *anode*. This indicates that these electrovalent hydrides contain the negative hydrogen ion  $H^-$ .

### Occlusion of Hydrogen. Alloy Hydrides

There are some metals—particularly platinum and palladium—which under certain conditions can absorb relatively large volumes of hydrogen. According to Thomas Graham (1867-9), palladium will absorb 935 times its own volume of hydrogen in cooling from a red heat, and at ordinary temperatures, 276 times its volume. The actual amount absorbed depends upon the physical condition of the metal. According to G. Neumann and F. Streintz (1892), one volume of the following finely divided metals will absorb the following volumes of hydrogen:

Palladium black . . . . .	502.3	Nickel . . . . .	15.6
Platinum sponge . . . . .	49.3	Copper . . . . .	4.5
Gold . . . . .	46.3	Aluminium . . . . .	2.7
Iron . . . . .	19.2	Lead . . . . .	0.1

The hydrogen is given off when the metal is heated, particularly under reduced pressure, and this property of palladium furnishes a useful means of weighing, and also of purifying, hydrogen gas. It was used by Morley in his work on the combining weights of oxygen and hydrogen (page 109).

Palladium increases in volume during the absorption, but its general appearance and properties are not much altered, although a considerable amount of heat is evolved during the absorption. Graham called the phenomenon **occlusion** (from *occludo*, I shut up). The gas is said to be occluded by the metal. It was formerly believed that a chemical compound was formed, but it is now thought that this is not so, although the exact relation between the occluded hydrogen and the metal is not certain.

It is now believed that there are three steps in the process of occlusion of hydrogen by palladium. The first is *surface adsorption* (page 259), probably accompanied by dissociation into atoms of hydrogen. This is followed by *rift diffusion* (diffusion along the inter-granular spaces of

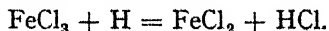
the metal) and finally diffusion from these rifts into the interstices in the crystal lattice of the metal (*lattice diffusion*). This results in the hydrogen atoms taking up positions in the lattice without displacing metal atoms so that an *interstitial compound* is formed.

### Reducing Action of Hydrogen

The readiness with which hydrogen will combine with oxygen and certain other non-metals makes it able very often to remove oxygen and chlorine from their compounds with the other elements. Thus, when hydrogen is passed over heated ferric oxide, lead oxide, nickel oxide, copper oxide, etc., the hydrogen combines with the oxygen of the oxide and leaves behind the metal. In these experiments, the hydrogen is said to be *oxidized*; and the metallic oxide, *reduced*, or deoxidized. (See Chapter 21, page 345, for a fuller discussion of the terms "oxidation" and "reduction.") Direct reduction with ordinary hydrogen in this way usually requires a high temperature, which limits the usefulness of the method, but hydrogen generated in the body of the liquid to be reduced will often bring about reduction where ordinary hydrogen bubbled through the solution will not. (See below—nascent hydrogen.) Also numerous reductions can be effected by passing a mixture of hydrogen and the vapour of the substance to be reduced over finely divided metals such as nickel (see pages 260, 936).

### Nascent Hydrogen

Hydrogen at the moment of its formation is more chemically active than ordinary hydrogen. For instance, ordinary hydrogen can be passed into an acidified solution of ferric chloride without producing any appreciable change, but if metallic zinc be placed in the solution, the brisk evolution of hydrogen is soon attended with the reduction of the ferric chloride to ferrous chloride.



Chlorates can be reduced to chlorides similarly:



Hydrogen prepared and acting in this way has been termed **nascent hydrogen**, i.e., hydrogen at the moment of birth.

It was at first suggested that the activity of nascent hydrogen is because at the moment of liberation it exists as single atoms, whereas in ordinary hydrogen the atoms have combined to form molecules  $\text{H}_2$ . The latter molecules will require work to be done on them to separate them into single atoms before they can react, while the single atoms of nascent hydrogen are ready at once and require no further work to be done on them before reaction can take place.

This theory is very attractive at first sight, but does not account for all the facts; in particular, the different degrees of reactivity of

nascent hydrogen made from different reagents. Thus, for example, chlorates are reduced to chlorides by the nascent hydrogen made from zinc and dilute sulphuric acid, but not by that which results when the action of sodium amalgam on water is used. Similar differences have been observed in the reducing power of the hydrogen evolved by electrolysis when using different metals as cathode, which suggests that these phenomena may be connected and so be capable of a single explanation.

It has been shown that in electrolysis those metals whose use as cathode require the highest voltages in order to bring about liberation of hydrogen yield hydrogen of the greatest activity. Thus, to obtain hydrogen by the electrolysis of dilute sulphuric acid with a lead cathode requires a voltage 0.49 volt higher than that required with a silver cathode (cf. page 233) and, in general, the higher the over-voltage, the greater the activity of the hydrogen formed. It seems, therefore, as though some of the extra energy supplied has become associated with the hydrogen, thus enhancing its chemical activity.

Similarly, it may be that the difference between nascent hydrogen formed in different reactions is due to the difference in the energy changes involved in these reactions. Energy is liberated as a result of the reaction producing the hydrogen, and this may not always all appear as heat but may become associated with the hydrogen being formed which is thus more reactive than ordinary hydrogen.

Another suggested explanation of the behaviour of nascent hydrogen is that at the moment of production the gas will be in the form of very minute bubbles, the internal pressure of which will be very great on account of their small size. Now it has been shown by Ipatiev that by the application of great pressure the activity of ordinary hydrogen can be increased and it may well be that this is connected with the behaviour of nascent hydrogen.

It is not possible in the present state of our knowledge to decide definitely between these theories except to say that the simple atomic hydrogen hypothesis is not so much favoured as formerly.

### § 5 Formula and Atomic Weight of Hydrogen

The atomic weight of hydrogen and its formula have been discussed in detail in Chapter 5 (page 82) and Chapter 7 (page 109). The combining weight has been determined by various investigators by measurements, with the most elaborate precautions, of the composition of water, both by weight and (in conjunction with the known densities of the gases) by volume. The number of atoms in the molecule has been inferred from observations on the combination of hydrogen and chlorine (pages 82, 541) and from measurements of the specific heats of hydrogen.

The accepted value for the atomic weight of hydrogen at present is 1.008 and its formula is  $H_2$ .

## § 6 Forms of Hydrogen

### Ortho- and Para-hydrogen

According to the latest conclusions about the structure of the atom (see Chapter 10, page 139), the hydrogen atom consists of a nucleus of mass 1 carrying a unit positive charge (i.e., a proton) and one electron. Consequently, the hydrogen molecule, which as mentioned in § 5 comprises two atoms of hydrogen, contains two protons and two electrons. It has been shown theoretically that such a molecule should be capable of existing in two forms, differing in the relation between the spins of the two nuclei. In one form the spins are in the same sense, and in the other in opposite senses (Fig. 20.4). These forms were named ortho- and para-hydrogen respectively and their existence has been confirmed by the partial separation of hydrogen into two forms.

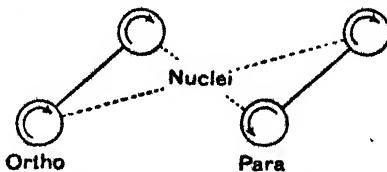


FIG. 20.4.—Ortho- and Para-Hydrogen

Ordinary hydrogen is an equilibrium mixture of ortho- and para-forms (containing about 75 per cent of ortho-hydrogen at ordinary temperatures). Theoretical considerations show that there will be a relatively large amount of heat evolved when the ortho-form is converted into the para-form, and hence it follows, from Le Chatelier's principle (page 248), that the equilibrium proportion of the latter will be greatest at low temperatures. By the application of these facts, Bonhoeffer and Harteck (1929) were able to prepare almost pure para-hydrogen by keeping hydrogen at liquid air temperature and 350 atmospheres pressure for a week. Practically pure para-hydrogen can also be obtained by the adsorption of hydrogen on charcoal at the temperature of liquid air. Ortho-hydrogen has not yet been obtained pure.

These two forms of hydrogen differ in certain physical properties, e.g., specific heat. Also the melting-point of para-hydrogen is given as  $-259.28^{\circ}\text{C.}$ , whereas that of ordinary hydrogen is  $-259.24^{\circ}\text{C.}$  Ortho- and para-hydrogen are sometimes spoken of as allotropic forms of hydrogen.

### Active Hydrogen

By subjecting hydrogen at ordinary temperatures to the action of a silent electric discharge, at an electrical pressure exceeding 30,000 volts (cf. formation of ozone, page 348), an active variety of hydrogen is obtained. It is marked by considerable chemical activity; thus, for example, it will combine directly, at ordinary temperatures, with lead or sulphur, forming hydrides, and will reduce cupric and ferric oxides in the cold.

It has been suggested that this "active-hydrogen" consists either of molecules  $\text{H}_2$ , or of single atoms, but neither of these explanations has been widely accepted, and it is generally regarded as an active form of ordinary hydrogen  $\text{H}_2$  (see active nitrogen, page 425).

### Atomic Hydrogen

Atomic hydrogen can, however, be produced by subjecting hydrogen to very high temperatures such as that of the electric arc; as was shown by Langmuir (1912). He also showed that this dissociation is brought about when hydrogen is in contact with a heated tungsten wire. The combination of two hydrogen atoms to form a hydrogen molecule is attended with the evolution of a very large amount of heat. Consequently the heat produced by the combustion of atomic hydrogen is very great, for the total heat evolved by the combustion of atomic hydrogen will be equal to the normal heat of combustion of molecular hydrogen *plus* the heat energy of formation of a molecule of hydrogen from its atoms. This fact is made use of in the atomic hydrogen blowpipe (see below, page 298).

### § 7 Isotopes of Hydrogen

It has been mentioned in Chapter 10 (page 140) that isotopes of an element have identical nuclear charges, but different atomic masses. The ordinary hydrogen atom consists of a nucleus with unit mass and unit charge, with one electron rotating round it. The simplest isotope of this atom would have a nucleus of mass 2, charge 1, and 1 electron as before. Whereas in general the isotopes of one element differ very slightly indeed in their ordinary properties, since a difference of one or two units represents only a small fraction of the total weight of the atom, in the case of hydrogen the differences to be expected are considerable in view of the relatively large difference in the weights of the atoms of the two isotopes.

The discovery of the heavy isotope of hydrogen, now known as **Deuterium** and represented by the symbol D, was the result in the first place of a discrepancy between the value of the atomic weight of hydrogen—as determined by physical and chemical means. The value obtained by the improved mass-spectrograph method of Aston was 1.0078, taking oxygen = 16.00 as standard. The best chemical value was also 1.0078, and as at this time oxygen was thought to be a "pure" element (i.e., to have no isotopes), the agreement between the two methods left nothing to be desired. The discovery in 1929 that ordinary oxygen contains two isotopes of mass 17 and 18 respectively showed that this agreement was more apparent than real, and the view was soon put forward that it must be a consequence of the presence of a small quantity of a heavy isotope in hydrogen also. Consequently a search for it was begun, and before long its existence was confirmed.

A spectroscopic examination of the residues remaining after the evaporation of large quantities of liquid hydrogen revealed faint lines corresponding to an isotope of hydrogen of mass 2 (Urey, 1932). About the same time Washburn and Urey examined the water from some commercial electrolytic cells which had been in operation for a number of years and found that it contained a larger proportion of "heavy" hydrogen than ordinary water. This observation gave the clue to a method of preparing "heavy" water and hence "heavy" hydrogen in quantity.

The method was applied by G. N. Lewis to the preparation of almost pure "heavy" water. He started with 20 litres of water in which the heavy-water content had already been somewhat increased by electrolysis, and continued the electrolysis of this until only 1.5 c.c. of liquid remained. This sample then contained approximately 66 per cent of heavy water. By combining the products of several such electrolyses and continuing the process, there finally resulted about 1.3 c.c. of almost pure  $D_2O$ .

Heavy water can also be obtained by fractionation, quite a large separation resulting when water is distilled, using a long fractionating column and working at a reduced pressure.

From the almost pure heavy water, heavy hydrogen itself can be obtained and finally purified by diffusion.

The chemical properties of deuterium are analogous to those of ordinary hydrogen as it enters into all the reactions characteristic of the latter, forming completely analogous compounds, but the rates at which corresponding reactions occur and the positions of the points of equilibrium differ considerably as might be expected. In general, deuterium reacts more slowly and less completely than ordinary hydrogen; it also exists in ortho- and para-forms.

Heavy water differs markedly from ordinary water in physical properties. A comparison of some of these properties is given in Table XXVII. In addition to these properties the solubilities of some substances is considerably less in heavy water than it is in ordinary water.

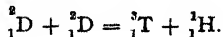
TABLE XXVII.—PROPERTIES OF WATER

	Ordinary Water	Heavy Water
Melting Point . . . .	0°	3.802°
Boiling Point . . . .	100°	101.42°
Specific Gravity . . . .	1.0	1.10764
Temperature of Max. Density . . . .	4°	11.23°
Surface Tension (at 20°) . . . .	72.75 dynes	72.8 dynes
Refractive Index . . . .	1.3329	1.3284
Viscosity . . . .	10.9	12.6
Dielectric Constant . . . .	82.0	80.5

The chemical differences between  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  and between  $\text{H}_2$  and  $\text{D}_2$  have been the subject of much investigation. One of the most interesting facts which has emerged is the ready interchange of hydrogen atoms which it indicates. Thus, for example, a solution of ammonium chloride in heavy water on evaporation yields a solid containing the same proportion of heavy hydrogen as was present in the water used. Again, if sugar is dissolved in heavy water *half* the hydrogen atoms of the sugar are exchanged for heavy hydrogen.

A similar phenomenon is observed when heavy hydrogen is kept over water for some weeks. The volume of the gas remains unchanged although all but about 5 per cent of it is replaced by ordinary hydrogen.

The existence of a third isotope of hydrogen of mass 3 has also been reported. The abundance of this third isotope (to which the name Tritium has been given) in ordinary water is estimated as 7 parts in  $10^{10}$ . It has been detected in artificial transmutation experiments (page 166), e.g., in the bombardment of deuterium with deuterons.



### § 8 Uses of Hydrogen

Hydrogen finds increasing employment in modern industrial operations, but the most important uses at present are in the manufacture of synthetic ammonia (see page 429) (although for this purpose it is

not isolated—cf. page 429) and for the hydrogenation of oils (page 260). It is becoming increasingly important for the production of "oil from coal" by hydrogenation of the coal (page 386) in presence of a catalyst such as ferric oxide, mixed with alumina and a little titanium oxide. It is also required for the production of tungsten filaments for electric lamps (page 880) and large quantities have been used for the filling of balloons since it is the lightest-known gas and its lifting power is considerable.

Hydrogen burns readily in air or oxygen and when used in the oxy-hydrogen blowpipe gives a very hot flame (about 2800°). This instrument was once widely used, but it has now been largely replaced by the oxy-acetylene blowpipe (see page 377). But it is still employed for fusing quartz and silica (e.g., for the manufacture of mercury vapour lamps), and for melting platinum. It is also used (sometimes as an *air*-hydrogen blowpipe) for the autogenous soldering of lead, for use in situations (such as the lead chambers used in sulphuric acid manufacture, page 496) where ordinary soldered joints would be readily corroded. The edges of the pieces of lead to be joined are welded by melting the edges together by means of the air- (or oxy-) hydrogen blowpipe. The flame is very suitable for this purpose since it is hot and yet reducing in character.

Another form of blowpipe known as the **atomic hydrogen blowpipe** has also found employment in certain welding operations. As mentioned above (page 295), atomic hydrogen is formed when an arc struck between tungsten electrodes is allowed to burn in an atmosphere of hydrogen. By blowing a jet of ordinary hydrogen across such an arc, the intensely hot flame, which results on account of the formation of atomic hydrogen, can be directed on to any suitable spot. This flame is capable of melting tungsten (which requires a temperature of 3400°), and a feature of its use is the great rapidity with which a surface can be heated—an important factor in welding operations. Owing to the reducing character of the flame, iron or alloys can be melted without fear of oxidation, and contamination with other elements, such as carbon (which sometimes occurs with the oxy-acetylene flame) is readily avoided.

### § 9 The Position of Hydrogen in the Periodic System

The position to be assigned to hydrogen in the Periodic System is not easily decided. As was pointed out in Chapter 9 (page 132), it does not easily fit into the general scheme. It has sometimes been placed at the head of Group I of the Table (the alkali metals), and though in view of its electropositive nature it is better classified with these elements than with any other group, this position is not entirely satisfactory. For although like them it has a powerful affinity for non-metals, and little or none for metals, and in its compounds with the former often forms electrolytes (acids) which bear resemblances to the corresponding salts of the alkali metals, it nevertheless is certainly



not to be thought of as a metal. On the other hand, as mentioned on page 292, when fused lithium hydride is electrolysed, hydrogen is liberated at the anode, just as chlorine is in the electrolysis of fused chlorides. To this extent, hydrogen resembles the halogens, though it is scarcely to be thought of as a halogen. In fact, the atomic structure of hydrogen (a nucleus carrying one positive charge and one electron) differs so markedly from that of any other element that it is justifiable to accord to it a special place in the Periodic Table and not to associate it with any particular group. This is what is done in the form of the table given on page 127.

The chemical behaviour of hydrogen, which forms compounds with many other elements, can be accounted for by the accepted structure of its atom.

Most hydrogen compounds result from the formation of covalent links whereby the hydrogen atom becomes associated with two electrons and so acquires the configuration of the helium atom. Compounds such as water, hydrogen chloride (anhydrous), ammonia, and hydrocarbons fall into this category. On the other hand, with highly electropositive elements, such as the alkali metals, hydrogen forms ionic compounds owing to the formation of hydrogen ions; again a configuration corresponding to that of helium results when it is in the form of an hydroxonium ion (page 269).

A third type of compound, characterized by the presence of hydrogen bonds (page 320), is sometimes found in combination with nitrogen, oxygen or fluorine.

It may be noted that the elements which form covalent compounds with hydrogen are those with an electronegativity (page 159) of 1.6 or more; those whose electronegativity is less than 1.0 form electrovalent compounds and the three elements which form hydrogen bonds have electronegativities of 3.0, 3.5 and 4.0 respectively.

### § 10 Water. Composition

The older chemists considered water to be an element. They were quite right so far as their knowledge went, because they did not know how to decompose it into simpler substances.

Priestley has told us that in 1776 his friend, J. Warltire, noticed that when a flame of hydrogen was allowed to burn in air confined under a bell-jar, the whole of the receiver appeared to be filled with a white powdery substance, and when the flame went out, the air left in the jar was perfectly noxious. In the same year P. J. Macquer inquired whether the flame of hydrogen evolves soot or smoke, and he thus described his experiment:

By placing a saucer of white porcelain in a jet of inflammable gas burning tranquilly at an orifice, I found that the part of the saucer which the flame licked was moistened by small drops of liquid as clear as water, and which, in fact, appeared to be nothing but pure water.

It is probable that J. Warltire's white cloud was nothing but condensed steam. In the spring of 1781, J. Priestley made what he called "a random experiment" to "entertain a few philosophical friends," in which a mixture of "inflammable air" with oxygen or atmospheric air was exploded in a closed vessel by means of an electric spark. The sides of the glass vessel were found "bedewed" with moisture after the explosion, but Priestley paid no particular attention to the phenomenon. H. C. Cavendish looked upon the deposition of the dew as a fact "well worth examining more closely," and immediately followed up the subject, in 1781, by exploding a mixture of "one measure of oxygen with two measures of inflammable air (hydrogen)" in a closed vessel. No gas remained in the globe after the explosion, but the hydrogen and oxygen lost their gaseous form, and produced a certain weight of water. The vessel and its contents underwent no change in weight, or parted with anything ponderable during the explosion, whilst a certain volume of gas was replaced by a certain weight of water. Hence, Cavendish deduced that **liquid water consists, weight for weight, of the hydrogen and oxygen gases lost in its production.** He thus established the fact that water consists of hydrogen and oxygen only, united in the proportions of two to one by volume approximately.

Cavendish's experiment has been repeated from time to time, with the introduction of all possible refinements in order to secure an accurate figure for the volume composition of water. Notable examples are the work of Scott, and of Burt and Edgar, which have been described already (pages 74, 110).

Experiments of this kind serve to establish the composition of water *synthetically*; corresponding *analytical* evidence was forthcoming soon after the time of Cavendish's experiment.

W. Nicholson and A. Carlisle, May 2, 1800, happened to put a drop of water in contact with two wires from an electric battery and noticed the formation of small bubbles of gas about the tips of the wires when the tips of the wires were not in contact. They then immersed the two wires in a glass of water, and found that gases were formed about both wires. They found the gas collected at one wire to be hydrogen, and at the other wire, oxygen. Two volumes of hydrogen were collected for every volume of oxygen. The gases were mixed and exploded. The result was water.

Nicholson and Carlisle's experiment is often repeated in the following modified form. The apparatus employed is illustrated in Fig. 20.5 and is usually called a **water voltameter**. It consists of two glass tubes *A* and *B*, terminated at the top by stopcocks, and connected near the bottom by a horizontal tube, to which is also attached a third vertical tube *C*, which ends in a reservoir *D*. The electrodes *E*, *E*, consist of pieces of platinum foil. Pure water is a very poor conductor, and so the experiment is carried out by filling the apparatus with water to which a little sulphuric acid has been added. A current is passed through the

solution by connecting the electrodes to an accumulator or other source of direct current. During the passing of the electric current, bubbles of gas from the metal plates rise into the glass tubes. Approximately twice as much gas is given off at one plate as the other. The gas in each tube can be examined. In the gas from one tube, a taper burns with the "blinding brilliance" characteristic of oxygen; and the gas from the other tube burns with the blue flame characteristic of hydrogen. Some of the water has disappeared, but no change can be detected in the amount of sulphuric acid mixed with the water. Hence it is inferred that the water, not the acid, has been decomposed. The experiment succeeds equally well if a very dilute solution of sodium or potassium hydroxide be used with nickel or iron electrodes. Here again the water, not the alkali, is decomposed.

A mixture of one volume of oxygen and two volumes of hydrogen, called **electrolytic gas** or **detonating gas**, if wanted in gas analysis, is easily provided by placing both electrodes under one receiver. Electrolytic oxygen contains a little ozone and hydrogen peroxide if prepared by the electrolysis of acidulated water, but not if a solution of barium hydroxide be electrolysed.

The information derived from these experiments did not, by itself, establish the formula of water for, as explained in Chapter 5, no relation between the combining volumes of gases and the number of atoms uniting was then known.

Crude attempts were made to discover the *weights* of hydrogen and oxygen combining together to form water, by multiplying the volumes found by Cavendish by the densities of the gases. But with the comparatively primitive types of apparatus then available the results were very inaccurate.

A determination of a different kind was made by Dumas in 1843. Although its accuracy is inferior to that of more modern experiments, it was far superior to any which preceded it and it was the forerunner of accurate atomic-weight determinations. The experiment illustrates some important principles, and it is therefore here described in outline.

It depends upon the fact, already noted (page 293), that when the oxides of such metals as iron, copper or lead are heated in a current of hydrogen, water is formed and the oxide is reduced to the metal.

If a known amount of copper oxide be employed, and the water formed be collected and weighed, the weight of the reduced copper oxide will show how much oxygen has been used in forming a definite amount of water. This was done by Dumas in 1843. The hydrogen

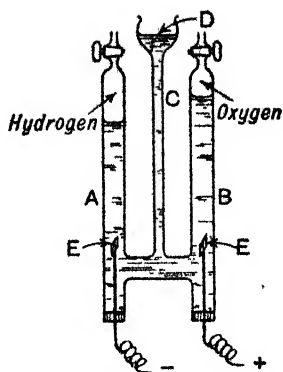


FIG. 20.5.  
Water Voltameter

was prepared by the action of zinc on sulphuric acid. Thus prepared the gas may contain nitrogen and oxygen derived from the air; sulphur dioxide and hydrogen sulphide derived from the reduction of the sulphuric acid by the hydrogen, carbon dioxide, arsenic hydride (if the acid or the zinc contained arsenic); hydrogen phosphide (if the zinc or the acid contained phosphorus); nitrogen oxides (if the acid contained nitrogen oxides); and water vapour. Accordingly, Dumas used sulphuric acid, which had been well boiled to get rid of dissolved air, and then passed the hydrogen through a series of U-tubes—Fig. 20.6—containing:

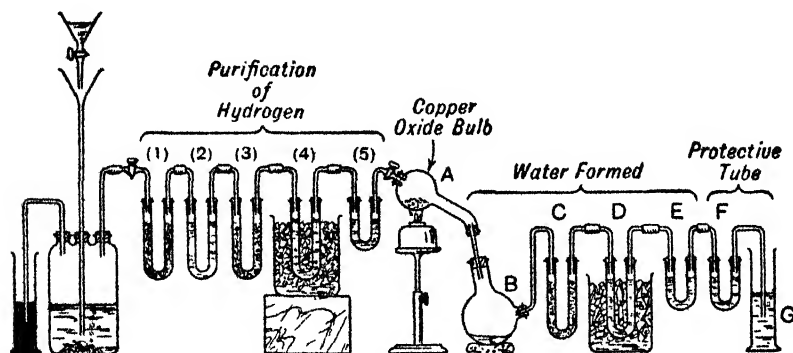


FIG. 20.6.—Dumas's Experiment (abbreviated)

(1) pieces of glass moistened with lead nitrate to remove hydrogen sulphide; (2) glass moistened with silver sulphate to remove arsenic and phosphorus compounds; (3) solid potassium hydroxide to remove sulphur dioxide, carbon dioxide, and nitrogen oxides;\* and (4) phosphorus pentoxide to remove moisture† not absorbed by the solid potassium hydroxide. The phosphorus pentoxide tubes were placed in a freezing mixture. The tube marked (5) in the diagram contained phosphorus pentoxide. It was weighed before and after the experiment. If no change in weight occurred, it was assumed that the hydrogen passing through was quite dry.

*The experiment.*—The purified hydrogen was passed through a weighed bulb *A*, containing copper oxide, and heated by the spirit lamp underneath. Most of the water condensed in the bulb *B*, and the remainder was absorbed in the U-tube *C*, containing solid potassium hydroxide, and in *D* and *E* containing phosphorus pentoxide. The phosphorus pentoxide tube *D* was kept cool by a freezing mixture. The three tubes, *C*, *D* and *E*, and the bulb *B* were weighed before and after the experiment. The last U-tube *F*, containing phosphorus

\* Dumas used three potassium hydroxide tubes, and two phosphorus pentoxide tubes. Only one of each is shown in the diagram.

† Ibid.

pentoxide, was followed by a cylinder *G* of sulphuric acid through which hydrogen escaped. The vessels *F* and *G* were not weighed; they served to protect the other tubes from the external atmosphere.

*The results.*—The average of nineteen experiments by Dumas gave:

Copper oxide lost in weight	44.22 grams
Water produced	49.76 grams
Hydrogen (by difference)	5.54 grams

Hence, every 16 parts by weight of oxygen combined with 2.004 parts by weight of hydrogen to form water. There is a curious error in Dumas's experiment which, if not corrected, makes the result a little high. The reduced copper retains some hydrogen very tenaciously (see occlusion of hydrogen by the metals, page 292). Other objections to Dumas's experiment have been made: (1) the expulsion of the air from the large apparatus is difficult (the U-tubes used were a metre long); (2) the air absorbed by the sulphuric acid is slowly evolved along with the hydrogen when the acid acts on zinc; (3) the copper oxide is contaminated with nitrogen absorbed from the air; (4) the slight reduction of sulphuric acid by hydrogen, forming gaseous sulphur dioxide; and (5) the complete drying of the hydrogen is very difficult. In approximate work we may take it that 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen to form 18 parts of water.

Dumas himself believed that the true value of this ratio should be 1 : 8; in fact, as is now known, his value was itself too high. The generally accepted value, based on Morley's work (see pages 109–11), is 1 : 7.94 or 1.008 : 8.

Up to about 1860 it was assumed that the formula for water was  $\text{HO}$  and hence, the atomic weight of hydrogen being unity, that of oxygen is 8 approximately. This gave satisfactory results in many respects for the formulae of other substances and the equations for reactions correctly indicated the proportions by weight of the elements in molecules of compounds and the weights of materials taking part in reactions.

But this formula for water, and the consequential formulae and atomic weights of other compounds and elements, rendered difficult of explanation the volume relationships between reacting gases. Avogadro's hypothesis gave the clue to the solution of the problem, but it was not until 1857 that, in the hands of Cannizzaro, it was properly applied and then very quickly accepted. It was then recognized that the molecules of hydrogen and oxygen must each contain two atoms, and that the formula of water is  $\text{H}_2\text{O}$ . The difficulties which had existed in any attempt to correlate the results of experiments on the combining volumes of gases with their densities and molecular weights disappeared; and observations such as that just described in the electrolysis of water, whereby two volumes of hydrogen result for one of oxygen, became easily explicable. This matter has already been discussed in some detail in Chapter 5.

An experiment performed by Gay-Lussac in 1808, and repeated by Hofmann in 1865, and which showed clearly the volumetric composition of steam, helped also to confirm the formula  $\text{H}_2\text{O}$  for water.

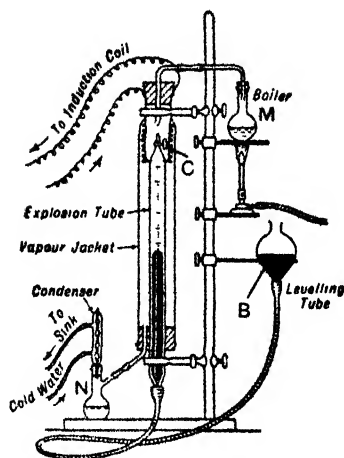


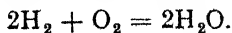
FIG. 20.7.—Synthesis of Steam by Volume

The apparatus used (Fig. 20.7) consists of a graduated explosion tube fitted with platinum electrodes, between which a spark can be passed, maintained at  $130^\circ$  by means of a jacket through which the vapour of boiling amyl alcohol is passed from the flask *M*. This vapour is condensed in the condenser *N*, so that the amyl alcohol is recovered. The explosion tube is filled with mercury by adjusting the levelling tube *B* and the stopcock *C*. A dry mixture containing one volume of oxygen and two volumes of hydrogen is introduced into the explosion tube via the stopcock *C* by depressing the levelling tube. When the explosion tube is about half or three-fourths filled and the amyl alcohol is steadily boiling the volume of its contents is read by

bringing the mercury to the same level in both levelling tube and explosion tube. Then the pressure of the gases is reduced as much as possible by lowering the levelling tube and sparks are passed between the electrodes. The gases explode forming steam. In a few minutes, when the temperature in the explosion tube is again constant the levelling tube is raised and the volume of the gas remaining measured at atmospheric pressure. It is found that the steam occupies just two-thirds the original volume of the mixed gases. On allowing the apparatus to cool to room temperature it is found that the mercury fills the explosion tube, showing that all the hydrogen and oxygen have combined to form water.

Hence, it is inferred that **when water is synthesized at a temperature above the point of condensation— $100^\circ$ —two volumes of hydrogen react with one volume of oxygen to form two volumes of steam.**

If we adopt Avogadro's Hypothesis, it follows that two molecules of hydrogen and one molecule of oxygen form two molecules of water (or steam). Hence, if hydrogen is  $\text{H}_2$  and oxygen  $\text{O}_2$  (see page 336),  $\text{H}_2\text{O}$  is the only possible formula for steam, i.e.,



### § 11 Occurrence of Water

It has been estimated that three-fourths of the surface materials on the crust of the earth is water. Animals and plants contain a large proportion of combined water—e.g., fish contains the equivalent of about 80 per cent; beef, 60–62 per cent; the human body, 70 per cent; aquatic plants between 95 and 99 per cent; and ordinary land plants, 50–75 per cent. A great many rocks contain water—combined and absorbed. Clay, for example, contains up to 14 per cent of combined water.

**The circulation of water in nature—the water cycle.**—Water is widely distributed in its three states of aggregation—steam or aqueous vapour, liquid water, and solid ice and snow. All the water on the earth passes through a remarkable cycle of changes. The heat of the sun leads to the evaporation of water from the seas, etc.; water vapour is only 0.62 times as heavy as an equal volume of air, and consequently it rises into the upper regions of the atmosphere, as well as diffusing into and mixing with atmospheric air. The temperature of the ascending vapour gradually decreases, and consequently a plane must be reached where the air is saturated with moisture. The vapour will then condense in the form of fine drops of water—mist or clouds. The fine drops coalesce into larger drops. Ultimately, the condensed water must descend again to the earth as rain, snow, or hail. The wind distributes the vapour. The heat given up during the condensation of the vapour is distributed or carried from the hotter regions—where evaporation is fastest—to the colder regions—where the vapour is condensed—thus helping to “stretch” the temperate regions nearer to the poles. The water which is sprayed, as rain, etc., on the surface of the globe, does a certain amount of physical and chemical work. On the chemical side, water helps in the decomposition and weathering of rocks; and on the physical side, it transports matter in suspension from the higher to the lower levels. The soluble matters ultimately collect in the seas.

Thus the water cycle involves: (1) evaporation from the oceans, seas, lakes, etc.; (2) condensation in the upper regions of the atmosphere as a fine mist of distilled water where it collects as clouds; (3) further condensation is followed by rain; (4) the rain water percolates through the soil and collects on an impervious bed of rock to be again forced to the surface, as spring water, by the pressure of the superincumbent layers; and (5) this is collected by the streams and rivers. The rivers return whence they came—to the sea, and commence anew the never-ending cycle. It must be added that a relatively small proportion of the water which finds its way into the ground falls out of the cycle since it is fixed by reaction with certain silicates and rocks forming hydrated silicates, hydrated alumino silicates, etc.

### Rain Water

"No water," said T. Bergman, "is ever found on the surface of the earth in a state of purity." Rain, in its journey through the air, dissolves oxygen, carbon dioxide, and nitrogen, as well as ammonia and ammonium nitrate. It also carries down dust—organic and inorganic. Rain water, particularly if collected near the sea in high winds, contains sodium chloride; and if collected near towns, sulphur compounds—sulphur dioxide and sulphuric acid—derived from the products of combustion of coal. When evaporated to dryness, 10,000 parts by weight of rain-water will give about 0.34 part of solid matter, most of this consisting of sodium chloride and organic matter. Rain water contains in solution about 0.013 per cent of dissolved nitrogen, 0.0064 per cent oxygen, and 0.0013 per cent carbon dioxide. The rain which falls at the end of a shower is more pure than that which falls at the beginning, because the atmosphere is washed, so to speak, during the earlier part of the shower.

### Spring and Mineral Water

Directly the rain water strikes the ground, it begins to attack and dissolve various rocks, decaying organic tissue (humic compounds), forming *surface and ground water*. It is estimated that between 25 and 40 per cent of the rainfall, in temperate regions, soaks into the ground. In its journey underground—*underground water*—the percolating water loses most of its organic matter and dissolves more or less mineral matters—compounds of calcium, magnesium, and sodium—and also dissolves carbon dioxide. The greater the depth to which the water sinks the greater the amount of solid matter it can dissolve. Water under great pressure is a powerful solvent. Sooner or later the water which has percolated underground will be forced to the surface as *spring water*. If the spring water holds an unusual amount of some particular constituent in solution which gives it a marked taste, or some specific property, the term *mineral water* is applied. Mineral waters do not necessarily contain a large excess of mineral matters in solution. The water from mineral springs is often named according to some special constituent dissolved in the water, or from the locality of the spring. "Fresh water" is a vague term applied to a natural water which does not contain much dissolved impurity.

### River Water

Spring water collects in rivers and streams. It has been estimated that the rivers of the world discharge some 6524 cubic miles of water into the ocean per annum. Rivers contain not only the solid matter furnished by spring waters, but also organic matter derived from plants growing on the sides and bottom of the river, and also from the drainage of villages and towns through which the river passes. The river, in virtue of its volume and force, carries along a considerable



amount of suspended solids. River water also contains in solution matter from the country which it drains. Thus the water of the Dee (Scotland), draining slate and sandstone rocks, contains about 0.0056 per cent of solid matter, about one-fourth of this being calcium salts; the Thames, draining chalk rocks, contains about 0.03 per cent of solid matter, two-thirds of which is calcium salts.

### Sea Water

Just as spring water flows into the rivers, the rivers flow into the sea carrying their dissolved salts, and suspended matters which have not been deposited in transit. The vapour which rises from the sea by evaporation is almost pure water; hence, unless the dissolved matters are continuously removed, sea water must be gradually getting more and more "salty." Sea water contains a relatively large proportion of soluble salts\*—about 3.5 per cent of solids in solution. Where the evaporation is greatest we naturally expect to find the greatest proportion of salts in solution. Thus the Mediterranean contains about 3.4 per cent of solids in solution; whereas the Baltic, with its numerous tributaries, and less evaporation, contains between 0.3 and 0.8 per cent of solids in solution. Salts accumulate in land-locked seas and lakes much faster than in the open sea. In illustration, the Dead Sea contains 22.8 per cent of solids in solution; the Great Salt Lake (Utah), 23 per cent; and the Elton Lake (Russia), 27 per cent. These masses of water behave as if they were exposed in a large evaporating basin, for the salts accumulate in the water and are deposited in crystalline masses on the shores of the lakes as the water evaporates.

### § 12 Purification of Water for Town Supply

Potable water, that is, water which is fit for human consumption, is obtained principally from rivers and lakes, and also from wells—artesian and otherwise. The inorganic or mineral matters usually found in solution in natural water are not directly injurious to health. The purification of water for towns and cities is a very important practical problem for the chemist. The best solution can only follow after a careful study of the local conditions. Water should be free from pathogenic (disease-producing) bacteria, and from suspended impurities. This is generally achieved by filtration through large filter beds made from layers of sand and gravel, extending in some cases over an acre of ground. Suspended and colloidal matter is now usually removed by adding aluminium sulphate which causes coagulation of the suspended matter and the formation of a bulky flocculent precipitate of

\* For instance, an average type contains about 96.5 per cent of water; 2.7 per cent of sodium salts; 0.07 per cent of potassium salts; 0.14 per cent of calcium salts; 0.59 per cent of magnesium salts, as well as dissolved gases; 0.012 per cent of nitrogen; 0.006 per cent of oxygen; and 0.017 per cent of carbon dioxide.

aluminium hydroxide. Most of the bacteria which may be present in the raw water are removed in this way; but for safety, especially where the supply is drawn from a river which, as for example, in the Thames Valley, may suffer contamination from inhabited areas higher up the valley, sterilization by means of chlorine is often utilized. A concentration of chlorine of three parts per million is usually sufficient to destroy all bacteria in a short period of time.

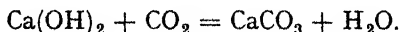
To maintain the purity of the water supply up to the proper standard, it is necessary to make (1) a periodical critical examination of the source from which the water is obtained; (2) regular bacteriological examinations for pathogenic germs; and (3) chemical examinations for nitrogenous organic matter—albumenoids, etc.—upon which bacteria feed, and for the products of bacterial life—free ammonia, ammonium nitrate and nitrite. The presence of these substances in water throws it under suspicion.

### § 13 Hard Water

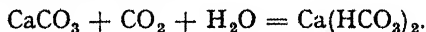
Water which will only with difficulty give a lather with soap is called **hard** water. The difficulty of obtaining a lather is due to the presence in the water of substances which react with the soap and form an insoluble precipitate. Water containing in solution salts of calcium or magnesium or of any metal other than the alkali metals or ammonium, behaves in this way.

The commonest cause of hardness is the presence of calcium salts, usually the bicarbonate or sulphate, or both; but the corresponding magnesium salts also occur.

It is a familiar fact of chemistry that the action of carbon dioxide turns lime-water "milky." Lime-water is a solution of slaked lime in water, and although slaked lime is only sparingly soluble in water it yet has a measurable solubility. The action of carbon dioxide on the lime-water is to convert the slaked lime (or calcium hydroxide) which it contains into calcium carbonate which may be reckoned to be insoluble:



If, after the lime-water has thus been rendered turbid through the precipitation of calcium carbonate, more carbon dioxide is passed, the solution will go clear again. This is owing to the formation of calcium bicarbonate which is a soluble salt.



This experiment gives the clue to the formation of one kind of hard water—that whose hardness is caused by the presence of calcium (or magnesium) bicarbonate (magnesium carbonate behaves similarly). Rain water absorbs carbon dioxide both from the air through which it falls and from decaying vegetation on the ground, and this water, thus charged with carbon dioxide, can dissolve calcium carbonate or

magnesium carbonate if it flows over rocks composed of these substances, owing to the formation of calcium or magnesium bicarbonate.

These bicarbonates are easily decomposed by heat with the re-formation of the normal carbonate. This process is complete at the boiling point of water, so that a sample of hard water whose hardness is caused by the presence of these bicarbonates has the hardness removed by boiling. Such water is said to exhibit **temporary** hardness. Hardness which is caused by substances such as calcium sulphate is not removed by boiling and is known as **permanent** hardness.

Hard water is then so called on account of the difficulty of getting a lather with it with soap. Soap is a compound of sodium with a fatty acid. The soap is decomposed by magnesium or calcium salts. The fatty acid unites with the latter to form an insoluble curdy precipitate. This action continues until all the calcium and magnesium salts have been precipitated. Any further addition of soap at once produces a lather, and the soap can then be used as a cleansing agent. If a solution of soap of definite strength and a definite volume of water be employed—and this can be made by finding what volume of a given soap solution is required to produce a permanent lather with a solution of calcium chloride of known concentration—say equivalent to one gram of calcium carbonate per litre—the hardness of a given sample of water can be represented in terms of the amount of soap required to produce a lather—**T. Clark's soap test**. The hardness of water thus refers to the "soap-destroying power" of the water, and it is expressed in degrees. *Each degree of hardness corresponds with one grain of calcium carbonate, or its equivalent in other calcium or magnesium salts, per gallon of water.* Hardness is also expressed in parts of calcium carbonate, or its equivalent, per 100,000 parts of water.

**EXAMPLE**—6 ml. of a standard soap solution (1 ml. = 0.001 gram  $\text{CaCO}_3$ ) were required in titrating 50 ml. of water in order to produce a lather which persisted for 5 minutes after the bottle containing lather and soap solution had been well shaken. Hence, the water contained calcium and magnesium salts—bicarbonates, sulphates, nitrates and chlorides—equivalent to 12 grams of calcium carbonate by weight per 100,000 ml. of water. To convert this number into grains per gallon, multiply by 0.7. The result, 8.4, represents the number of grains of calcium carbonate per gallon of water. The hardness of the water on Clark's scale is therefore 8.4.

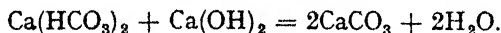
Waters containing but small quantities of calcium and magnesium salts lather freely with soap and they are accordingly called **soft waters**. A water of less than 5° hardness may be called "soft," and a water between 18° and 20° hardness is "moderately hard," and if over 30° hardness, "very hard." Very soft waters in the presence of oxygen and carbon dioxide act upon lead, forming lead hydroxide,  $\text{Pb}(\text{OH})_2$ , which is slightly soluble and poisonous. Such water, if used for drinking purposes, over a period of time may produce cumulative poisoning. Water which contains mineral carbonates or sulphates forms, by contact with lead, a protective coating of lead carbonate or sulphate and further action then ceases. Consequently it is usual for

water supply undertakings whose raw water is very soft to harden the water artificially.

Hardness in water is a cause of considerable waste and inconvenience. For washing purposes it induces great waste of soap, since no lather can be obtained until the calcium or other metal present has been removed by the soap. One of the advantages of the, so-called, soapless detergents (often referred to simply as "detergents") which have become popular in recent years, is that their action is unaffected by the presence of calcium and magnesium salts in the water. When temporarily hard water is boiled, the calcium and magnesium carbonates are deposited, often as a crust on the containing vessel. This is the cause of the formation of "fur" in kettles, and of scale in boilers. Methods for the removal of the hardness of water are thus of primary importance in all industrial work.

### § 14 The Softening of Water

The process of removing calcium salts from hard water is called **softening the water**. In the case cited above, soap is the softening agent. If the hardness of the water be caused by the presence of bicarbonates of calcium or magnesium, mere boiling will soften the water because, as indicated already, the acid carbonates are then decomposed, and the normal carbonates are precipitated. In **T. Clark's process for softening water** (1841), the necessary amount of milk of lime or lime-water is added to convert all the bicarbonates of lime and magnesium into the normal carbonate. This process depends upon the fact that the slaked lime reacts with the acid salt present in the solution to form normal calcium carbonate, which is precipitated. The carbon dioxide is thus removed from the bicarbonate present, calcium carbonate again being precipitated. These facts are expressed in the equation:



It is important to avoid adding excess of slaked lime as some of this will then dissolve, forming lime-water which is a permanently hard water and may well be very much harder indeed than the water which is being softened.

Magnesium carbonate is appreciably soluble in water and its solubility is too high for its presence to be tolerated in the feed water of modern boilers. The magnesium is therefore precipitated as hydroxide either by including sodium hydroxide in the chemicals used for treatment or by adding additional slaked lime equivalent to the magnesium present and then removing the calcium thus introduced, by means of an equivalent quantity of sodium carbonate.

Water, any part of whose hardness is temporary, may be softened by boiling. If the water also possesses permanent hardness, it may be dealt with as follows.

After removing the temporary hardness, if present, by boiling or by

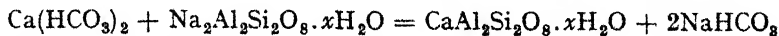
Clark's process, the permanent hardness may be removed by the addition of sodium carbonate. The boiling as well as the alkali carbonate processes of softening water were known towards the middle of the eighteenth century and were described by T. Bergman (1778). The sodium carbonate precipitates the calcium and magnesium as insoluble carbonate:



The water still contains sodium sulphate or sodium chloride, but the presence of a small quantity of these salts is not usually objectionable and it has no effect on soap which is also a sodium salt. Sodium carbonate will remove temporary as well as permanent hardness.

A process of water softening which is becoming increasingly important is the **permutit** or **base-exchange** process (Fig. 20.8). In this process the water is passed through a layer of powdered zeolite, either natural or artificial. Zeolites are complex aluminosilicates. The natural products used are usually *glauconites*; the artificial ones (e.g., *permutit*) are porous gels made by fusing a mixture of quartz sand, china clay, and soda ash or by mixing solutions of sodium aluminate and sodium silicate. The calcium and magnesium salts in the water react with the zeolite, forming insoluble calcium and magnesium zeolite, and a soluble sodium salt. This removes both temporary and permanent hardness. Iron and manganese salts are also removed by this process. The "exhausted" zeolite is revived by passing a concentrated solution of sodium chloride through it. The calcium and magnesium zeolite re-forms sodium zeolite.

The reactions taking place may be represented by the equations:



when softening is taking place, and



when the exhausted permutit is being regenerated.

Synthetic resins are now known which exhibit ion-exchange behaviour

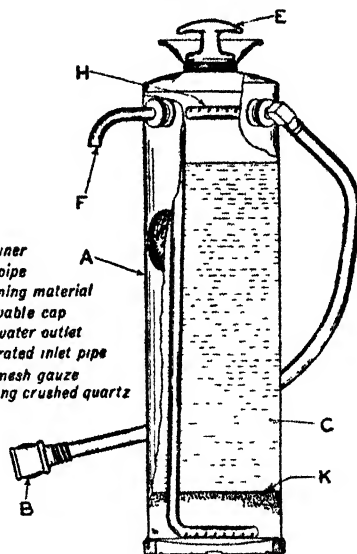
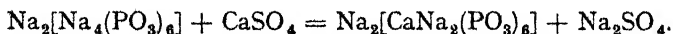


FIG. 20.8 —Permutit Type of Water Softener  
(By permission of the Electrolyx Co., Ltd.)

and which can be regenerated by dilute acid or dilute alkali. By this means water free from dissolved salts can be produced (cf. page 223).

Water can be softened on a small scale by adding so-called sodium hexametaphosphate (known commercially as *calgon*). This does not precipitate the calcium but removes the calcium ions from the water possibly by forming with them a complex ion which does not react with soap:



This view of the action of *calgon* is, however, said to lack experimental support and it has been suggested, as an alternative, that the calcium ions are adsorbed on colloidal particles of the polymerized "metaphosphate" (cf. page 827). In fact, the nature of the action is not known.

### Hard Water in Nature

Rain water percolating through limestone rocks becomes highly charged with dissolved calcium bicarbonate; such water in dripping through the roof of a cave or subterranean cavern will be exposed to the air; as a result, some carbon dioxide escapes from the solution, and a certain amount of calcium carbonate is deposited. Each drop of water adds its own little share of calcium carbonate. The deposit grows—maybe on the roof, when it is called a **stalactite**; maybe on the floor, when it is called a **stalagmite**. All depends upon the time occupied by each drop in gathering and dropping, how fast the carbonate is deposited. Measurements of a stalactite in the Ingleborough Cavern (Yorkshire), made in 1839 and 1873, show that it grew at the rate of 0.3 inch per annum. The San Filippo spring (Tuscany) is said to deposit "lime" at the rate of 12 inches a month and the spring has formed a bed of limestone rock 250 feet thick,  $1\frac{1}{4}$  miles long, and  $\frac{1}{8}$  mile wide. The stalagmite grows upwards from the ground, and the stalactite grows downwards, like an icicle, from the roof. In time, the two may meet and form a pillar. Plate 14 conveys but little idea of the beauty of some limestone caverns in which stalactites and stalagmites have been growing. The photograph shows stalactites, stalagmites, and pillars which have no doubt been formed in this manner. There are some very fine grottos, caves, or caverns in Castleton and other parts of Derbyshire, at Cheddar in Somerset, in the Isle of Skye, Antiparos (Archipelago), in the Hartz (Germany), Auxille (France), New South Wales, Auckland, United States, and numerous other limestone districts. The building stone called *travertine* (Tiber-stone) is probably a limestone deposited from a mineral spring. The Colosseum and much of ancient and modern Rome were built with this stone.

### § 15 Purification of Water for Scientific Purposes

The water supply of a town is watched, as has been said above, to ensure its fitness for drinking; but it is still far from being "chemically

pure," and so for many scientific purposes it is unsuitable. Two grades of water are ordinarily distinguished for laboratory work, viz.:

- (i) Distilled water;
- (ii) Conductivity water.

Distilled water can be made by means of an apparatus comprising a distilling flask and Leibig condenser, but partly on account of the slight solvent action of water on the glass, and partly because of the considerable quantities required in the average laboratory, some form of water-still designed for the purpose is usually employed. A great many have been devised for such work and electricity is now tending to supersede gas as the means of heating. It is important that the vessel, in which the water is boiled, should be so arranged in relation to the condenser that no spray is carried over by the steam as it enters the condenser. The condenser should, preferably, be made of pure tin or, at least, be heavily plated with tin if it be made of some other metal.

Distilled water prepared in this way is pure enough for most chemical work, but for the investigation of matters such as the conductivity of solutions, it is still not pure enough. The yet purer water required for these purposes is known as conductivity water, and its preparation has already been described (page 222).

## § 16 Properties of Water

### Physical Properties

At ordinary temperatures, pure water is a tasteless and odourless liquid; it is colourless in moderately thin layers, but appears greenish-blue when viewed in thick layers. According to J. Aitken, the blue colour of large bodies of water—e.g., in china-clay settling pits, in tanks in which water is being softened by the addition of milk of lime, etc.—is an optical effect due to the action of the fine particles suspended in the liquid on the light.

Liquids are but slightly compressible. If 1000 c.c. of water be subjected to a pressure of two atmospheres the volume will be reduced by 0.05 c.c. Nevertheless, according to P. G. Tait, this very small compressibility means that if sea water were quite incompressible, the average level of the sea would be raised 116 feet higher than it is today, and 4 per cent of the present land surface would be submerged.

Non-metallic liquids are bad conductors of heat; water is one of the best of liquids for conducting heat (mercury excepted), but even then the thermal conductivity is small.

Water boils at 100° under 760 mm. pressure. The greater the pressure, the higher the boiling point; and conversely, the smaller the pressure,\* the lower the boiling point. These phenomena occur with liquids generally, and it is therefore necessary to state the pressure when giving the boiling point of a liquid. If no pressure is stated

\* Roughly about  $\frac{1}{3}$ ° C. per mm. for a few degrees above and below 100.

760 mm. is understood. Thus at Quito (9350 feet above sea-level), with the barometer at an average height, 525.4 mm., water boils at  $90.1^{\circ}$ ; and on the top of Mount Everest (29,002 feet), barometer at 255.3 mm., water would boil at  $72^{\circ}$ . Steam or water vapour is an invisible, colourless gas which condenses to a visible cloud of small particles when it comes in contact with the atmosphere. This is readily shown by boiling water in a flask; inside the flask, the vapour is invisible, and a cloud of minute water particles—condensed steam—appears where the steam comes in contact with the cold air.

Liquid water freezes at  $0^{\circ}$  into crystalline ice. Water vapour freezes into hoar frost and snow. The crystals can often be seen when a piece of ice is examined with a lens while a beam of bright light is passed through it. Snow crystals are common. They appear in the form of a hexagonal (six-sided) nucleus or six-rayed star with the rays developed in bewildering complexity. The crystals are of inimitable delicacy and beauty. No two seem alike; but all are fashioned after one definite type—the six-rayed star. Ice appears to be colourless or white when pure, but it is pale blue when seen in large masses.

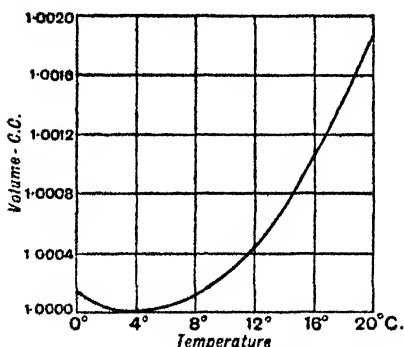


FIG. 20.9—Relations between the Volume and Temperature of Water

By plotting the volume of a given mass of water at different temperatures, we get a curve similar to that illustrated in Fig. 20.9. This curve shows that, at temperatures above  $4^{\circ}$ , water, like most liquids, expands when heated and contracts when cooled down to  $4^{\circ}$ ; but the curve below  $4^{\circ}$  is abnormal. It shows that water expands when cooled below, and contracts when heated up to  $4^{\circ}$ . If the specific gravity of water at  $4^{\circ}$  be taken as unity, it follows that water becomes specifically lighter when the temperature is raised or

lowered beyond this point. The expansion of water when cooled from  $4^{\circ}$  to  $0^{\circ}$  is very small, but that minute quantity has a very important bearing in nature. When the water on the surface of, say, a lake is cooled, it contracts. The heavier cold water sinks, and the warm water rises. This circulation cools the temperature of the whole body of water down to  $4^{\circ}$ ; any further cooling results in the formation of specifically lighter water. Accordingly, this remains on the surface, and circulation ceases. Finally, as a result of this remarkable and abnormal property, when the temperature of the atmosphere falls to  $0^{\circ}$ , a surface film of ice is formed.\* If the water did not expand in this way, as the temperature

\* "Ground ice" or "anchor ice" is formed at the bottom of rapidly moving streams when the water is thoroughly mixed and does not settle in layers.



fell to 0°, the whole body of water would freeze from below upwards and produce profound climatic changes, since the larger amount of ice formed in winter would materially affect the temperature for the rest of the year. These remarks do not apply to sea water which contracts as the temperature is lowered down to the freezing point. In the act of freezing water expands so that 100 c.c. of liquid water at 0° gives approximately 110 c.c. of ice at the same temperature. The specific gravity of ice at 0° varies with its mode of formation from 0.9159 to 0.9182; the specific gravity of water at 0° is 0.999867. Accordingly, ice floats on the surface of water. The expansion of water during freezing is an important factor. The expansion may burst the inter-cellular tissue of plants by freezing the cell-sap; the expansion may disrupt the fibres of flesh, so that frozen meat appears rather more "pulpy" than ordinary meat. If water freezes in pipes, the expansion of water in the act of freezing may burst the pipe, and the pipe will "leak" when the ice "thaws"; water freezing in the surface crevices of rocks splits and widens the fissures so that the surface crust of the rock appears to disintegrate during a "thaw." The debris collects as "talus" at the foot of the rocks, ready to be transported by water to lower levels. Hence this simple force plays an important part in the weathering and decay of rocks, building stones, etc., in countries exposed to alternate frost and thaw; and J. Tyndall adds: "The records of geology are mainly the history of the work of water."

The electrical properties of water have been mentioned already in Chapter 15 (page 222). It is a poor conductor of electricity, having a specific conductivity at 25° C. of only  $0.043 \times 10^{-6}$  mhos. It is, however, notable in being a good *ionizing* solvent, that is to say, compounds like common salt and hydrochloric acid, i.e., electrovalent compounds, dissolve in it, giving conducting solutions in which the solute has become largely dissociated into ions. Water is not the only ionizing solvent known, but it is the best.

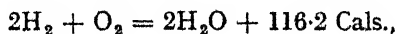
It has been observed that solvents whose dielectric constant (or specific inductive capacity) is highest are the best ionizing solvents, and this is in agreement with what would be expected on the basis of the electronic theory of valency, according to which electrovalent compounds, such as sodium chloride, are united, in the solid state, by the electrical forces between the ions (cf. Chapter 11, page 155).

### Chemical Properties

The chemical properties of water can be classified broadly under three main headings, viz., (i) reactions in which water undergoes decomposition; (ii) reactions in which water acts as a catalyst; (iii) reactions in which water forms addition compounds.

#### *Decomposition Reactions*

The combination of hydrogen and oxygen to form water is attended with the evolution of a large quantity of heat, as indicated by the equation:

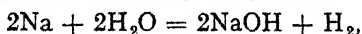


the water formed remaining as steam. It therefore follows, by the application of the principle of Le Chatelier, that if the reaction is to any extent reversible, the dissociation of the steam into hydrogen and oxygen will occur most at high temperatures. Investigation shows that dissociation does in fact take place, but it is difficult to carry out such an experiment since the decomposition only takes place at high temperatures, and recombination occurs very rapidly when the temperature is lowered, so that the formation of oxygen and hydrogen is not easily detected. Table XXVIII gives some values of the dissociation at various temperatures.

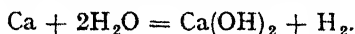
TABLE XXVIII.—THERMAL DISSOCIATION OF WATER

Temperatures	Degree of Dissociation (per cent)
1124°	0.0073
1288°	0.034
1984°	0.77
2369°	4.3
2488°	8.6
2656°	11.1

Many elements which are higher in the electrochemical series than hydrogen will, as pointed out on page 286, decompose water at a suitable temperature. The alkali metals (sodium, potassium, etc.) attack water readily at the ordinary temperature:

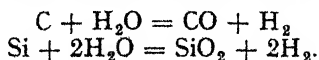


and the alkaline earth metals (calcium, strontium, etc.) behave similarly:

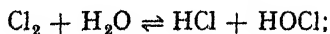


Magnesium, however, is only slightly affected by cold water, but reacts fairly readily with hot water. Magnesium, zinc and iron readily react with steam. Aluminium does not react with water in ordinary circumstances, since it is protected by a surface film of oxide, but if this is removed and some means adopted for preventing its re-formation, aluminium will decompose water in the cold. This can be effected by amalgamation with mercury.

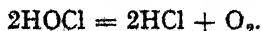
Non-metals for the most part do not react with water; the exceptions being carbon and silicon, and fluorine and chlorine. Carbon at a white heat decomposes steam, forming water-gas (see pages 400-1), and silicon reacts similarly, but much more slowly:



Chlorine, when passed into water, first dissolves, forming a green solution, but on standing, reacts, forming hydrochloric and hypochlorous acids:



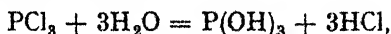
in sunlight the latter acid breaks up with the formation of oxygen:



Fluorine acts somewhat similarly, but no intermediate stage can be detected, and hydrofluoric acid and oxygen (mixed with ozone) are obtained in all circumstances:



Reactions involving water, but in which hydrogen is not evolved are, of course, very numerous, and plentiful examples occur in later chapters. Among these mention might now be made of **hydrolytic** reactions, that is to say, the decomposition of a compound by means of water. Examples are the hydrolysis of the halides of non-metals, such as the phosphorus halides:

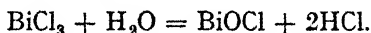


in which the halogen is removed as its hydracid and the corresponding hydroxy derivative of the non-metal is formed. A similar reaction occurs with substances such as sulphuryl chloride (the acid chloride of sulphuric acid).



$\text{SO}_2(\text{OH})_2$ , otherwise  $\text{H}_2\text{SO}_4$ , is, of course, sulphuric acid.

Salts which are derived from acids and bases of markedly different strengths are generally hydrolysed in aqueous solution (see Chapter 18). In some cases a basic salt is formed; for example, bismuth trichloride is hydrolysed to bismuth oxychloride:



### § 17 Water as a Catalyst

The remarkable catalytic activity of water has been alluded to in Chapter 17 (page 259), but calls for more extended consideration here.

Isolated experiments, going back to the latter half of the eighteenth century, had shown that some chemical reactions proceed more readily in the presence of water than in its absence, but real knowledge of the subject begins with the observation of Dixon in 1880 that a mixture of carbon monoxide and oxygen which had been dried for some time over sulphuric acid did not explode on passage of a spark, although after the addition of the merest trace of water to the mixture a violent explosion occurred when a spark was passed.

Further investigations along the same lines, by H. B. Baker, revealed several other reactions, normally taking place with explosion, or at least with the liberation of a great deal of energy, which are inhibited by the intensive drying of the reactants; and later, and perhaps yet

more remarkable, he claimed that intensive drying has in many cases a pronounced effect on the physical properties of substances.

Baker's investigations have shown that the *complete* drying of any substance or substances is a difficult task, particularly as minute traces of water are retained by surfaces such as those of the glass vessels in which the experiments are carried out. In order to remove these traces, it is necessary to heat them in a stream of perfectly dry air. The intensive drying demanded in order to achieve Baker's results is effected by prolonged exposure of the gases, or liquids, concerned to phosphorus pentoxide by sealing them up in tubes for a period of some months or even years.

Among the reactions which are inhibited or slowed down enormously by complete drying, the following may be mentioned. Carbon only combines with oxygen very slowly on heating; ammonia and hydrogen chloride do not combine on mixing; sulphur and phosphorus may be distilled in perfectly dry oxygen. Hydrogen and chlorine and hydrogen and oxygen will not explode when perfectly dry.

As regards this last reaction, Baker made the remarkable observation that perfectly dry hydrogen and oxygen, when mixed and heated almost to the melting point of silver, do not combine; but that a spark will cause combination to take place to some extent but *without* explosion. Further, although after the passage of a spark the sides of the tube can be seen to be covered with dew, still no explosion can be brought about. It has been suggested that the water formed is too pure to catalyse the reaction.

Ammonium chloride, which dissociates when heated in the ordinary way, was reported by Baker to be capable of vaporization without dissociation if intensively dried. Much controversy has taken place concerning the theoretical implications of this result; but in 1929 Rodebusch and Michalek claimed that Baker's conclusion was due to a faulty method of density measurement.

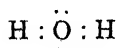
It is now believed that, although perfectly dry ammonium chloride does undergo dissociation in the same way as "ordinary" ammonium chloride, it only volatilizes very slowly. In consequence, in a Victor Meyer apparatus, even after a considerable time, some solid may remain when the measurement of the vapour is made, thus leading to a high result for the vapour density.

As regards the effect of moisture on the physical properties of substances Baker found that, after several years' drying with phosphorus pentoxide, many liquids had their vapour pressure reduced and their boiling point and surface tension increased. The melting points of solids such as iodine and sulphur were similarly found to be raised.

These results have been disputed in some quarters and the question is still *sub judice*, but for the moment it is necessary to accept the accuracy of Baker's work although it is very difficult to explain its results.

### § 18 Addition Compounds of Water

Water exhibits a marked tendency to form additive compounds with other substances of the kind sometimes called **molecular compounds**. This property is believed to be due to the electronic structure of the water molecule, which may be represented:



and which thus contains two "lone pairs" of electrons which can form co-ordinate linkages (see Chapter 11, page 157).

The most important of these compounds are the hydrates—particularly salt hydrates. Very many salts, when crystallized from water, yield crystals which contain water combined in simple molecular proportions. Familiar examples are washing soda,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , and ordinary blue copper sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . These compounds lose their water (often known as **water of crystallization**) on heating, but the different molecules of water are often held with varying tenacity. Thus, for example, copper sulphate crystals lose four molecules of water at a temperature very little above  $100^\circ$ , whereas a temperature in excess of  $200^\circ$  is required to drive off the fifth. (Cf. Fig. 17.1, page 246.)

It is thought by some that the water molecules are attached to the ions of the salt by co-ordinate valencies, and that in the case of copper sulphate one molecule is attached to the sulphate ion, whereas the other four are attached to the copper ion, thus accounting for the difference in the strength of attachment. This may be so, but we really know very little beyond the simple facts that: (1) water is a product of the dissociation of the hydrates; (2) water is usually given off at comparatively low temperatures; (3) water is not an essential part of the reacting unit in its most characteristic transformations; and (4) water is not generally necessary for the formation of the salt since water of crystallization can generally be removed by suitable means leaving the salt anhydrous. Several zeolites may lose their combined water and take it up again without losing their crystalline form.

If the term "water of crystallization" be carelessly employed, it may suggest that crystallization is somehow dependent on the presence of water, and this the more, as efflorescent salts *appear* to lose their crystalline character when water is lost. Crystals of gypsum— $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ —form a white chalky powder when the water is driven off; crystalline sodium carbonate, and also Glauber's salts, likewise produce white powders when their combined water is expelled. The powdered dehydrated substances are all crystalline. In fact, practically all chemical compounds can be crystallized. Crystallization is not dependent upon the presence of water. Sulphur, common salt, iodine, potassium chlorate, potassium sulphate, and numerous other crystalline substances do not contain the elements of water. Again, crystalline

calcespar does not contain the elements of water, and yet when calcined it gives a white powder. The calcespar has lost carbon dioxide, not water.

Related to this property of water of forming additive compounds is the fact that, in ordinary circumstances, liquid water is *associated*, that is, its molecules are probably more complex than is indicated by the formula,  $H_2O$ . Water is so frequently represented by this formula that it is easy to forget that in all probability it does not accurately represent liquid water. The evidence for these statements may be summarized as follows:

(i) Steam has a vapour density just above its boiling point, which is higher than that corresponding to  $H_2O$ ;

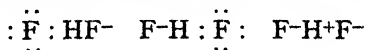
(ii) water boils at  $100^\circ$ , whereas hydrogen sulphide, its analogue (page 483), which would be expected to have a higher b.p. than water, boils, in fact, at  $-61^\circ$ ;

(iii) many of its physical properties, such as its high surface tension, high dielectric constant, show departure from the values to be expected if it were not associated.

### The Hydrogen Bond

The phenomenon of the association of water and of other similar liquids such as alcohol, formic acid, hydrogen fluoride and liquid ammonia as well as the structure of ice, in which each oxygen atom is surrounded by four others with a hydrogen atom between each pair, has made it clear that a hydrogen atom can, in certain circumstances, act as a link between two other atoms. Substances in which hydrogen is acting thus are said to contain a **hydrogen bond**. It appears that only nitrogen, oxygen or fluorine atoms can be linked in this way although a hydrogen bond can be formed between a dissimilar pair of these atoms.

Pauli's exclusion principle (page 148) makes it clear that a hydrogen atom can form only one covalent link so that the hydrogen bond must be essentially an ionic bond; since the proton is extremely small its electrostatic field must be correspondingly intense. A striking example of hydrogen bonding is furnished by the  $HF_2^-$  ion in which, on account of the highly electronegative character of the fluorine atom, the structure is that of a proton linking two fluorine ions by electrostatic forces; the  $HF_2^-$  ion is then represented  $F-H^+F^-$ . This ion is also sometimes represented as a resonance hybrid (page 160) of the three structures



of which the last is the most important.

Similar considerations apply to other compounds containing hydrogen bonds.

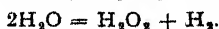
Apparently when hydrogen is covalently linked to an electronegative element the strong attraction of that element for the electrons binding

the hydrogen to it leaves the hydrogen with a positive charge which is great enough, as there are no screening electrons, to attract a second electronegative atom.

### § 19 Hydrogen Peroxide. Formation and Preparation

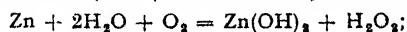
Hydrogen peroxide is a remarkable compound which was discovered by L. J. Thenard in 1818.

It is formed in small quantities in a variety of reactions. For example, it is formed when oxygen is bubbled about the electrode from which hydrogen is being evolved during the electrolysis of dilute acid, and also at the anode during the electrolysis of dilute sulphuric acid at a high current density. Water confined in a quartz vessel is decomposed by exposure to ultra-violet light rays—from a mercury lamp, sunlight, etc.—and hydrogen peroxide and hydrogen are formed:

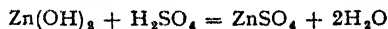


Hydrogen peroxide is produced during the combustion of hydrogen in air. For instance, when a jet of burning hydrogen impinges on the surface of cold water in which ice is floating, or on ice itself, hydrogen peroxide can be detected in the water; and is formed when moist ether is exposed to sunlight; and when ozonized oxygen or air is passed through water on the surface of which a little ether floats.

Like ozone (*q.v.*), hydrogen peroxide can be formed at a high temperature by passing a current of moist oxygen through a tube at about 2000° and rapidly chilling the issuing gases. It is often formed when a substance is oxidized in the presence of moisture. For instance, when zinc, copper, or lead is shaken up with air and dilute sulphuric acid (1 : 55), the reaction symbolized:



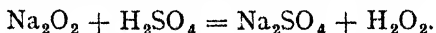
and



occurs.

In the laboratory hydrogen peroxide is made by the action of acids on certain peroxides, such as sodium peroxide (page 614) or barium peroxide (page 709).

By adding sodium peroxide in small quantities at a time to 20 per cent sulphuric acid, cooled in ice, hydrogen peroxide is produced:

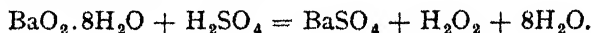


About two-thirds of the sodium sulphate formed crystallizes out with 10 molecules of water of crystallization, thus effecting a considerable concentration of the solution, which is decanted and distilled in vacuo. Phosphoric acid can be employed similarly when most of the salt separates as  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , the remainder being removed by cooling in a freezing mixture.

It is, however, not easy to separate hydrogen peroxide from soluble salts formed in its preparation; and so barium peroxide is the usual starting point as the barium can be precipitated as carbonate or sulphate.

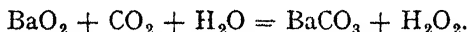
Anhydrous barium peroxide does not react readily with sulphuric acid because a coating of insoluble barium sulphate is formed. Consequently *hydrated* barium peroxide,  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ , is used. This is obtained by adding finely powdered commercial barium peroxide to

concentrated hydrochloric acid mixed with an equal volume of water and cooled in ice, until the acid has been neutralized. A little barium hydroxide solution is then added to precipitate any iron or aluminium present and the filtered solution is added to a saturated solution of barium hydroxide. Hydrated barium peroxide separates as a white crystalline precipitate. For the preparation of hydrogen peroxide the hydrated barium peroxide is added to ice-cold dilute sulphuric acid (1 vol. of acid to 5 vols. of water).



The barium sulphate is filtered off, leaving an approximately 20 per cent solution of hydrogen peroxide.

If barium peroxide is added slowly to ice-cold water through which a stream of carbon dioxide is passing, insoluble barium carbonate is precipitated, and a dilute aqueous solution of hydrogen peroxide remains:



This works well with anhydrous barium peroxide.

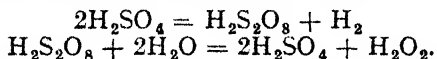
If an excess of carbon dioxide be used, the yield of hydrogen peroxide is low and an insoluble barium percarbonate,  $\text{BaCO}_4$ , is precipitated.

Until very recently hydrogen peroxide has been manufactured almost entirely by electrochemical methods. Three such processes have been operated on the technical scale, viz.:

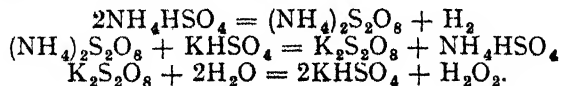
- (i) the persulphuric acid method;
- (ii) the potassium persulphate method; and
- (iii) the ammonium persulphate process.

The last-named is now the most important method although the potassium persulphate process was used on a large scale in Germany during the 1939-45 war.

The persulphuric acid method electrolyses approximately 10-normal sulphuric acid between platinum anodes and lead cathodes separated by a porous porcelain diaphragm. The persulphuric acid thus produced (cf. page 510) is hydrolysed to hydrogen peroxide by heating:



The potassium persulphate method depends upon the electrolysis of a solution of ammonium sulphate in sulphuric acid followed by precipitation of potassium persulphate by potassium bisulphate. Hydrogen peroxide is then obtained by distilling the potassium persulphate with dilute sulphuric acid:



The ammonium persulphate process involves the electrolysis of a



solution of ammonium sulphate (200 g. per litre) in sulphuric acid (300 g. per litre) in a stoneware bath with a platinum anode, a carbon or lead cathode with the cell divided down the middle by a porous diaphragm. Many attempts have been made to find an alternative material for the anode; so far without success. The persulphate liquor formed is then introduced into a special distillation unit in which it is fractionated under reduced pressure so as to give a solution of 30–35 per cent of hydrogen peroxide directly. This is the normal procedure in this country; by a suitable modification of the plant solutions of 50 per cent strength can be obtained.

A new method for the manufacture of hydrogen peroxide using an organic compound (2-ethylanthraquinol) which undergoes autoxidation in contact with the air, with the concomitant formation of hydrogen peroxide, has recently begun operation on a large scale. The reaction may be expressed by the equation



where  $A(OH)_2$  represents 2-ethylanthraquinol and  $AO_2$  its oxidation product. The latter can be reduced to the starting product by means of hydrogen in presence of a catalyst (palladium on an inert support).

The oxidation is carried out in solution in a suitable organic solvent; the hydrogen peroxide formed is recovered by extraction with water: the initial extract contains about 20 per cent of hydrogen peroxide.

The hydrogen required for the process is obtained by cracking butane from a nearby oil refinery in presence of steam and a catalyst. The carbon monoxide also formed is converted to carbon dioxide and removed as in the Bosch process (page 289).

Hydrogen peroxide of high concentration (i.e. 75 per cent or over) is now produced in large quantities by further fractionation processes. The successful production of these high concentrations depends upon the elimination of impurities during the earlier stages of manufacture since small traces of some impurities render hydrogen peroxide very unstable (cf. below).

By cooling a 95 per cent solution of hydrogen peroxide in solid carbon dioxide mixed with ether the whole mass solidifies, and if some of this solid be placed in a further sample of the 95 per cent hydrogen peroxide at  $-10^\circ$ , small needle-shaped crystals of pure hydrogen peroxide separate. (Maass, 1928.)

## § 20 Occurrence and Properties of Hydrogen Peroxide

### Occurrence

There is uncertainty about the alleged occurrence of hydrogen peroxide in rain, snow, dew, and air, as is indicated (page 354) in connection with the occurrence of ozone in air. Much of the published work does not clearly discriminate hydrogen peroxide from other oxidizing substances.

### Properties

Pure hydrogen peroxide is a viscid liquid; colourless when viewed in thin layers, but with a bluish tinge when viewed in thick layers. The liquid has no smell. Dilute aqueous solutions have a peculiar bitter metallic taste. When a drop of liquid peroxide comes in contact with the skin, it forms a white blister. If concentrated sulphuric acid be mixed with hydrogen peroxide at a low enough temperature to prevent heating, oxygen rich in ozone is evolved. The liquid decomposes rapidly when heated at ordinary atmospheric pressures, but under reduced pressure it can be readily distilled. It boils at  $69.7^{\circ}$  under a pressure of 28 mm., and at  $84-85^{\circ}$  under a pressure of 68 mm. The liquid crystallizes in needle-like prisms which melt at  $-1.7^{\circ}$ . The liquid is soluble in water in all proportions; dilute solutions are neutral but it behaves in some circumstances as a weak acid, as is indicated also by its conductivity and dissociation constant.

Pure hydrogen peroxide is fairly stable. Dilute aqueous solutions keep fairly well—particularly if acid; a 3 per cent solution suffered no appreciable change when kept a year. Alkaline solutions do not keep very well. Impurities like silica, iron, manganese, and alumina lead to a more rapid decomposition. If alcohol or ether be present, the aqueous solutions are more stable. The strength of aqueous solutions is represented commercially by the number of volumes of oxygen which 1 c.c. of the solution will furnish on decomposition. Thus 1 c.c. of a "10-volume solution" will give 10 c.c. of oxygen when decomposed. A 3 per cent solution of hydrogen peroxide is very nearly a "10-volume solution"; a 6 per cent hydrogen peroxide solution is nearly of "20-volume" strength, and so on. The commercial concentrated solution is called **perhydrol**, and it contains about 30 per cent of hydrogen peroxide, corresponding with a "100-volume" strength.

### Decomposition by Contact Action

Pure hydrogen peroxide is decomposed very rapidly if any dust be present. A little platinum black causes an explosion. Finely divided gold, silver, and similar metals, as well as powdered manganese dioxide, behave similarly. The action appears to be catalytic; a small trace of colloidal platinum, gold, etc., can accelerate the decomposition of large amounts of hydrogen peroxide. The action has been compared with that of yeast on a solution of sugar, and these "colloidal" metals have been given the name *inorganic ferments*.

A few drops of liquid hydrogen peroxide on a piece of cotton-wool will make the cotton inflame. Similar results are obtained with aqueous solutions of hydrogen peroxide, but the action is much less vigorous. Rough surfaces have a disturbing effect on the stability of hydrogen peroxide—a concentrated solution is decomposed when poured on to a ground-glass surface. The presence of small quantities of some substances—e.g., calcium chloride, alcohol, glycerol, acetanilide or barbituric

acid—makes the solutions more stable; these agents have been called *anticatalysts*, *negative catalysts*, or *retarders*. Acetanilide is particularly useful in preserving hydrogen peroxide solutions.

### Oxidizing Properties

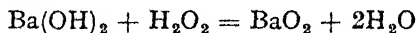
Hydrogen peroxide, as will be seen, resembles ozone in its strong oxidizing qualities. It liberates iodine from solutions of potassium iodine,  $\text{H}_2\text{O}_2 + 2\text{KI} = 2\text{KOH} + \text{I}_2$ . The reaction is accelerated by acetic and mineral acids, and particularly by ferrous sulphate. According to Schönbein, one part of hydrogen peroxide in the presence of 25,000,000 parts of water can be detected by a mixture of potassium iodide and ferrous sulphate. It converts black lead sulphide into white lead sulphate, as is also the case with ozone. Hence the use of hydrogen peroxide for cleaning oil paintings which have been darkened by the action of hydrogen sulphide—present in the air of towns—upon the lead compounds in the paint.

Hydrogen peroxide forms some addition compounds such as  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$  in which there appears to be an analogy with water of crystallization. A crystalline compound of this type with urea is made and sold commercially under the name **hyperol** and liberates hydrogen peroxide on solution in water.

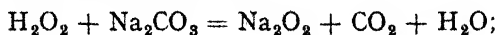
Dilute solutions of hydrogen peroxide are used for bleaching silk, feathers, straw, hair, ivory, teeth, etc., where more violent bleaching agents would injure the material. Instead of hydrogen peroxide an acidified solution of sodium peroxide is sometimes employed. The actions are similar. Since the products of the decomposition of hydrogen peroxide—water and oxygen—are harmless, it is also used medicinally and surgically as an antiseptic. Hydrogen peroxide is also used in analytical work for the oxidation of sulphates to sulphites; arsenites to arsenates; chromic salts to chromates; ferrous to ferric salts; nitrites to nitrates, etc. H. B. Baker and L. H. Parker showed that if hydrogen peroxide be removed from synthetic water, the water attacks sodium amalgam much more slowly than water containing, say, 1 part of the peroxide in 100,000.

### Peroxidizing Properties

Hydrogen peroxide forms peroxides of the alkalis and alkaline earths when treated with the corresponding hydroxides. For instance, with barium hydroxide:



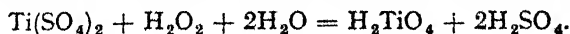
W. Spring (1895) pointed out that hydrogen peroxide behaves in these reactions like an acid (page 340). In confirmation, if sodium carbonate be added to hydrogen peroxide the corresponding alkaline peroxide is formed and carbon dioxide is evolved:



if the hydrogen peroxide be added to the solution of the carbonate, oxygen is evolved.

The sodium carbonate acts as a catalytic agent in the latter case. It is not at all uncommon to find reactions progressing differently according to the way the substances are mixed together.

With titanium salts, hydrogen peroxide gives an orange-yellow coloration supposed to be due to the formation of pertitanic acid:

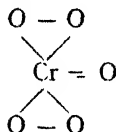


The particular tint depends upon the amount of titanium present, and hence the reaction can be used for the determination of the amount of titanium in various materials.

A solution of titanyl sulphate is made by heating titanium dioxide ( $\text{TiO}_2$ ) with twice its volume of concentrated sulphuric acid, cooling and diluting with cold water. A little of this solution is added to the solution suspected to contain hydrogen peroxide; a yellow or orange colour indicates its presence.

Cerium and vanadium salts give brick-red coloration, and uranium a bluish coloration, but these reactions are not so sensitive as with titanium salts.

With chromic acid,  $\text{H}_2\text{CrO}_4$ , hydrogen peroxide forms a blue solution which begins to decompose immediately with the evolution of oxygen. It was for long believed that the solution contains a perchromic acid, variously formulated but usually written  $\text{HCrO}_5$ , but evidence has now been brought forward which indicates that it is chromium pentoxide,  $\text{CrO}_5$ , or



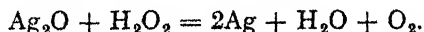
It is much more soluble in ether than in water, so that if a mixture of chromic acid and hydrogen peroxide in a test-tube be shaken with ether, a blue ethereal solution will float on the surface of the aqueous layer. The compound decomposes when the ether is evaporated. This reaction is used for the detection of chromates. It is said that this method will indicate one part of hydrogen peroxide in 80,000 parts of water.

### Reducing Properties

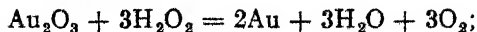
Hydrogen peroxide appears to act as a reducing as well as an oxidizing agent. With ozone it forms oxygen and water:



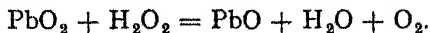
with silver oxide, metallic silver and oxygen:



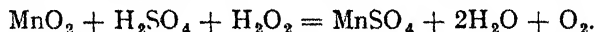
Similarly with gold oxide:



and lead dioxide,



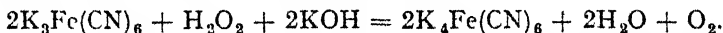
Curiously enough, in these reactions, the reducing agent is itself reduced—usually the reducing agent is oxidized during the reduction. The lead dioxide obtained when red lead is digested with dilute nitric acid does not dissolve, but if a few drops of hydrogen peroxide be added, all the lead dioxide dissolves in a few moments. The lead dioxide is reduced to lead monoxide by the hydrogen peroxide, and the product dissolves immediately in the dilute acid. This method is generally employed to bring about the solution of red lead in dilute acid prior to analysis. Hydrogen peroxide in alkaline solutions oxidizes manganous oxide,  $\text{MnO}$ , to manganese dioxide,  $\text{MnO}_2$ ; but in acid solutions it reduces manganese dioxide to manganous oxide:



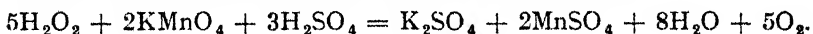
Also, whereas in acid solution hydrogen peroxide will oxidize potassium ferrocyanide to the ferricyanide:



in alkaline solution the reverse action occurs:



A solution of potassium permanganate— $\text{KMnO}_4$ —acidified with sulphuric acid is rapidly reduced by hydrogen peroxide:



Consequently, if an aqueous solution containing a known amount of potassium permanganate be run from a burette into a known volume of hydrogen peroxide until the pink colour of the permanganate is no longer discharged, the amount of hydrogen peroxide present can be calculated. This is a convenient method for the determination of hydrogen peroxide.

### Detection of Hydrogen Peroxide

A number of the reactions of hydrogen peroxide are similar to those of other oxidizing agents—particularly ozone (q.v.). It is necessary, in consequence, to be able to distinguish hydrogen peroxide from these other substances and also to be able to detect it in their presence. The actions of hydrogen peroxide on titanium sulphate and on chromic acid (*v. supra*) are distinctive, and hydrogen peroxide is also the only substance which will liberate iodine from potassium iodide in presence of ferrous sulphate. A table of distinguishing tests for ozone and hydrogen peroxide will be found on page 354 (Table XXIX).

### Uses of Hydrogen Peroxide

The earliest uses of hydrogen peroxide were concerned with the bleaching of textiles, particularly wool (which being nitrogenous is damaged by chlorine) and straw. It is now frequently applied to the bleaching of cotton also especially in the United States but its use for this purpose is increasing in this country. Hydrogen peroxide is used also for the production of organic compounds, such as glycols, from unsaturated compounds and for making perborates and percarbonates for use in washing powders, denture-cleaning compositions and similar preparations. The fact that hydrogen peroxide on decomposition, or in certain reactions, gives off oxygen and leaves only water has been utilized in the manufacture of porous materials such as "foam-rubber."

A large-scale use of hydrogen peroxide which has attracted much attention since 1939 is its employment for the propulsion of rockets and jet aircraft and for similar purposes. It can be used, as a fuel, either in its own right, or as a source of oxygen for the combustion of some other substance in the oxygen liberated by its decomposition. When used in the former way, the hydrogen peroxide is decomposed catalytically, with the release of oxygen gas and a considerable amount of energy along with steam. It is employed in this way in some forms of assisted take-off motor.

Two types of fuel can be used with hydrogen peroxide when the function of the latter is to supply oxygen. In one of these spontaneous ignition occurs when the two compounds are mixed, in the other a fuel is used which will not ignite unless the hydrogen peroxide is catalysed beforehand. An example of the former is a mixture of methyl alcohol, hydrazine hydrate and a trace of potassium cuprocyanide, which was used by the Germans in the V1 (flying bomb) and V2 rockets; the latter type uses kerosene (paraffin) or gasoline (petrol).

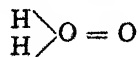
### § 21 Composition and Constitution of Hydrogen Peroxide

The composition of hydrogen peroxide was determined by Thenard, who introduced a weighed quantity into a graduated cylinder over mercury. He then decomposed it either by heat, or by adding manganese dioxide, and obtained about 8 parts by weight of oxygen and 9 parts of water from 17 of hydrogen peroxide. The empirical formula of hydrogen peroxide is thus HO.

The molecular weight of hydrogen peroxide has been found, from its vapour density (which is 17 at 90°), and from the freezing points of its solutions, which also indicate 34 as its molecular weight. Hence the molecular formula is  $\text{H}_2\text{O}_2$ .

There is still doubt as to the constitutional formula to be assigned to hydrogen peroxide. It was at first suggested that it is  $\text{H}-\text{O}-\text{O}-\text{H}$ , which is supported by the fact that hydrogen peroxide is formed in reactions involving the reduction of oxygen and not by the oxidation

of water. But in order to account for the instability of one oxygen atom, Kingzett (1884) suggested the formula



In terms of the modern electronic theory of valency, the maximum co-valency of oxygen is three, and so this would become  $\begin{array}{c} \text{H} \\ \diagup \\ \text{H} \end{array} \text{O} \rightarrow \text{O}$ , otherwise written  $\text{H} : \ddot{\text{O}} : \ddot{\text{O}} :$  or  $[\text{H} : \ddot{\text{O}} : \ddot{\text{O}}]^- \text{H}^+$ , which latter formula is

in agreement with the fact already noted that in some cases hydrogen peroxide behaves as a weak acid. Against this view, however, must be set the evidence of Baeyer and Villiger (1900) from organic reactions with hydrogen peroxide which clearly points to the dihydroxyl formula; but it is unsafe to attach too much importance to the structure of organic derivatives as evidence of that of the corresponding hydrogen compound.

The X-ray spectrum of pure liquid hydrogen peroxide, according to Randall (1937), indicates that the hydrogen atoms are arranged in directions at right angles to each other and to the line joining the oxygen atoms.\* (See Fig. 20.10.)

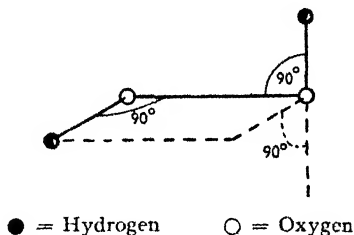


FIG. 20.10. —Structure of Hydrogen Peroxide

The reported discovery of a new variety of hydrogen peroxide formed by the action of atomic hydrogen on oxygen at liquid-air temperature (Geib and Harteck, 1934) suggests the existence of molecules of both types.

\* More recent work (Abrahams *et al.*, 1951) has suggested that the angle between the H—O and O—O bonds is 97° and that between the planes containing the hydrogen atoms is 94°.

## CHAPTER 21

### OXYGEN

On the first of August, 1774, I endeavoured to extract air from *mercurius calcinatus per se\** and I presently found that . . . air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it and found that it was not imbibed by it. But what surprised me more than I can well express was that a candle burned in this air with a remarkable brilliant flame.—J. PRIESTLEY.

#### § 1 History and Occurrence

THE discovery of oxygen must be accounted one of the most important advances in the history of chemistry, ranking along with the discovery of the composition of water. As has been said (page 5), air was for long considered to be an element, and it was not until the end of the eighteenth century that it was recognized to be essentially a mixture, the active constituent of which we now call oxygen.

Oxygen was discovered independently by Scheele some time between 1771 and 1773, and by Priestley in 1774. Scheele called the gas "fire-air" and "vital air," and made it by heating red oxide of mercury; sulphuric acid and manganese dioxide; nitre; and some other substances. Scheele did not publish an account of his work until 1777. Meanwhile, Joseph Priestley independently prepared the same gas, which he called "dephlogisticated air," while examining the effect of heat upon a great variety of substances confined in a cylinder (A,

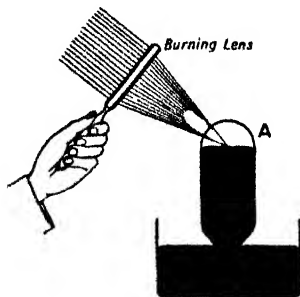


FIG 21.1.  
Priestley's Experiment

Fig. 21.1) along with mercury, and inverted in a trough of mercury, somewhat as in Fig. 21.1. Priestley focused the sun's rays upon the different substances by means of a "burning lens of 12 inches diameter, and 20 inches focal distance." Priestley announced his discovery of oxygen in the words quoted at the head of this chapter.

Many erring steps have stumbled on the threshold of the discovery of oxygen; for instance, Eck de Sultzbach, in 1489, knew that red oxide of mercury gave off a "spirit" when heated; had he named and isolated the "spirit" he would have been credited with the discovery of oxygen. In 1678, O. Borch prepared the gas by heating saltpetre; in 1727, S. Hales collected the gas obtained by heating saltpetre; P. Payen obtained it in 1774; and J. Priestley

\* That is, mercuric oxide, or red oxide of mercury.



himself obtained it the same year. These are not usually considered to have been discoveries of the gas because no attempt was made to determine the specific properties of the product. There are also indications in old books that the Greeks knew about oxygen in the fourth century; and that the Chinese were acquainted with the gas long before Priestley's and Scheele's experiments.

The real importance of this discovery escaped both Scheele and Priestley on account of their adherence to the doctrine of phlogiston, and it fell to Lavoisier to show that combustion, calcination of metals and respiration are related phenomena and are processes of combination with oxygen. The account of Lavoisier's work in this field belongs properly to the history of the elucidation of the nature of the atmosphere and is given elsewhere (Chapter 26).

### Occurrence

Oxygen is the most widely distributed and commonest of all the elements, comprising about 50 per cent of the earth's crust.

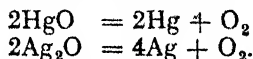
About one-fourth of the atmospheric air, by weight, consists of free oxygen, and water contains nearly 89 per cent of combined oxygen. Oxygen also forms a material part of rocks. Thus calcium carbonate, which occurs as chalk, limestone, marble, etc., contains 48 per cent of oxygen; and silica, which is found in flint, quartz, etc., contains over 53 per cent of oxygen by weight.

### § 2 Preparation and Manufacture of Oxygen

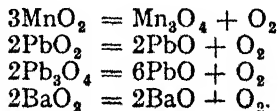
Oxygen is obtained either from the atmosphere, or by the decomposition of oxygen-containing compounds, such as oxides and salts of oxyacids. It is also formed along with hydrogen in the electrolysis of water.

The atmosphere is the only source of oxygen which is used for its manufacture (see below), but other methods are employed for its preparation in the laboratory. For experimental purposes, however, oxygen from a cylinder (obtainable commercially) is increasingly used.

Many oxides are not decomposed by heat, but some, notably those of the so-called "noble" metals (e.g., mercury, gold and silver), are decomposed in this way. Priestley's method of making oxygen from mercuric oxide exemplifies this fact and silver oxide behaves similarly:

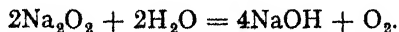


The higher oxides of some other metals lose oxygen on heating and a lower oxide remains. Examples are manganese dioxide, lead dioxide, red lead, barium dioxide:



These methods are not now of practical importance, although barium dioxide was formerly utilized for the commercial preparation of oxygen since it can be readily obtained by heating barium oxide in the air. (See Brin's process—below, page 334.)

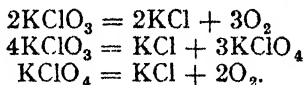
The peroxides of the alkali metals give off oxygen when brought in contact with cold water, and oxygen may be prepared conveniently in this way:



*Oxone* is a commercial preparation consisting of sodium peroxide mixed with a little catalytic agent like colloidal manganese dioxide, and is used for the making of oxygen on a small scale. The salts of some oxy-acids such as chlorates, permanganates and nitrates decompose when heated, yielding oxygen, and this is the basis of the ordinary laboratory method of preparing oxygen, potassium chlorate being the most convenient salt to use.

### Preparation of Oxygen from Potassium Chlorate

Potassium chlorate is a white crystalline solid which melts to a clear liquid when heated to about  $340^\circ$ . At about  $350^\circ$  the melted chlorate appears to boil, because bubbles of oxygen gas are copiously evolved. After a time the bubbling ceases and the molten mass begins to "thicken" or solidify. The potassium chlorate has decomposed into potassium perchlorate, potassium chloride, and oxygen. If the temperature be raised still further—over  $600^\circ$ —the mass again melts to a clear liquid and the potassium perchlorate decomposes, giving off more oxygen. The final products of decomposition are potassium chloride and oxygen. The reactions which take place may be represented:



The temperature required to drive off the whole of the oxygen is rather higher than is convenient for ordinary work, but the salt may be completely decomposed, at a much lower temperature, if it has been mixed with manganese dioxide.

After the action, manganese dioxide still remains, but the potassium chlorate has decomposed into potassium chloride and oxygen. Manganese dioxide can be recovered from the residue by lixiviating the mass with water. The water dissolves the potassium chloride, and leaves the manganese dioxide as a residue.

This is the traditional method for preparing oxygen in the laboratory but, when a cylinder is not available, it is now more usual to make it by the action of water on sodium peroxide. The sodium peroxide is placed in a flask, fitted with a tap funnel and delivery tube; the rate of formation of oxygen is then easily controlled by regulating the flow of water from the tap funnel.

The preparation from potassium chlorate consists in carefully heating a mixture of this salt (not powdered) with its own bulk of manganese dioxide\*—oxygen mixture—in a large test-tube, or a retort, or a special copper "oxygen tube," fitted with a wide delivery tube, because the gas is liable to come off rapidly in rushes. The tube is best clamped while tilted slightly downward towards the mouth, as indicated in Fig. 21.2, because a considerable amount of moisture is usually discharged from the mixture, and there is a risk of the moisture trickling back and cracking the glass. The gas is collected over water as in the case of hydrogen. The oxygen obtained by this process sometimes contains traces of carbon dioxide and chlorine. These can be removed by passing the gas through a soda-lime tube as shown in Fig. 21.2.

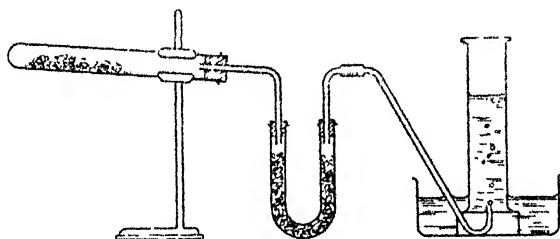
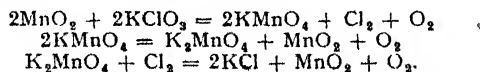


FIG 21 2 —Preparation of Oxygen

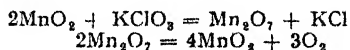
The action of the manganese dioxide in this experiment is curious. It was first observed by Dobernein in 1820 and has been referred to already in Chapter 17 as an example of a "catalytic agent," i.e., a substance which can accelerate (or retard) a reaction, without itself undergoing any permanent chemical change in the process. In the decomposition of potassium chlorate many other oxides act similarly, but are not quite so effective—e.g., ferric, copper, cobalt or nickel oxide may be used in place of manganese dioxide.

The exact way in which the manganese dioxide acts is still uncertain. One plausible idea is that potassium permanganate is alternately formed and decomposed as indicated in the following equations:



This view is supported by the fact that a trace of chlorine is often found in the gas produced in this way and the potassium chloride left is often coloured pink.

Other suggestions have been alternate formation and decomposition of a higher oxide of manganese, e.g.,



\* If the manganese dioxide contains carbonaceous matters, an explosion may occur. Hence the manganese dioxide should be tested by heating a *little* with potassium chlorate before a large quantity is heated. Pure, precipitated manganese dioxide should be used and not the "commercial" grades.

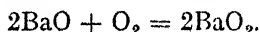
and that the manganese dioxide provides nuclei which prevent the supersaturation of the chlorate with oxygen.

The suggestion that the manganese dioxide does take part in the reaction chemically is borne out by the fact that if lumps are used to make the initial mixture they are found to have become finely powdered after the experiment.

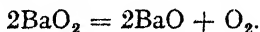
Many other methods are available for obtaining oxygen, as, for example, by heating sulphuric acid with manganese dioxide, chromium trioxide, potassium dichromate, potassium permanganate, or other salts rich in oxygen. A 10 per cent solution of hydrogen peroxide and a concentrated solution of potassium permanganate gives off oxygen when acidified with sulphuric acid. Potassium permanganate, when heated alone, also gives off some oxygen, and bleaching powder solution readily decomposes in presence of a cobalt salt (as a catalytic agent), yielding oxygen (cf. page 547).

### Manufacture of Oxygen

For the industrial preparation of oxygen the atmosphere is the only practicable source. Oxygen was formerly manufactured by Brin's process (1881) which depended upon the formation of barium dioxide when barium oxide is heated in air to about 500°:



If the barium dioxide be heated to a still higher temperature, 800°, or the pressure reduced without altering the temperature, the oxygen is given off and barium oxide remains as a residue:



The extraction of oxygen from liquid air is the method by which the whole of the oxygen of commerce is now manufactured. The fractionation of liquid air has been described on pages 48-52.

### § 3 Properties of Oxygen

Oxygen is, at ordinary temperatures, a colourless, tasteless, and odourless gas. It is a little denser than air. Oxygen is appreciably soluble in water—100 volumes of water, at 0°, can dissolve nearly 5 volumes of oxygen under a normal pressure of 760 mm., and at 20° about 3 volumes of the gas are dissolved. Fish are dependent upon the air dissolved in water for the oxygen they need for respiration. Animals are dependent upon the oxygen in air for respiration. Air normally contains 21 per cent of oxygen, and if the proportion falls to 17 per cent no known deleterious effects have been observed. Indians living in the upper reaches of the Andes breathe air which has oxygen equivalent to air with 12 per cent of oxygen at ordinary atmospheric pressure. When the proportion of oxygen falls below this value the air is getting dangerous and, although air with less than 7 per cent of oxygen can be breathed with impunity for a short time,

life will soon be extinguished. A mouse soon dies if placed in an atmosphere deprived of oxygen. Pure oxygen can be breathed for a short time without harm, and oxygen is used medicinally for the resuscitation of persons who have been suffocated, or suffering from carbon monoxide poisoning, etc., where, owing to the enfeebled action of the lungs, the blood is not sufficiently aerated; and where it is necessary to stimulate a person with an internal injury—e.g., a broken rib—which would prevent artificial respiration. The prolonged inhalation of oxygen soon raises the temperature of the body dangerously high. An animal placed in ordinary or in compressed oxygen soon dies.

Metallic silver, gold, platinum, and palladium absorb oxygen at about  $500^{\circ}$ . Molten silver dissolves about ten times its volume of oxygen, and gives it up again on cooling. In cooling, a solid crust forms on the exterior surface; as the interior cools the gas bursts through the solid crust driving out a spurt of the still fluid metal—the phenomenon is called the “spitting” of silver. Molten platinum behaves in a somewhat similar way.

Oxygen has been condensed to a bluish-coloured mobile liquid which boils at  $-183^{\circ}$  at 760 mm. The liquid has a specific gravity of 1.13. Liquid oxygen can be frozen to a pale bluish-white solid not unlike snow in appearance. The solid melts at  $-218.8^{\circ}$ , and has a specific gravity 1.43. The critical temperature of oxygen is  $-118.8^{\circ}$  and the critical pressure 49.7 atmospheres.

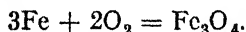
Liquid oxygen is strongly attracted by a magnet, so that if a little liquid oxygen is placed in a cup beneath the poles of an electromagnet, it leaps up to the poles and remains permanently attached until all is evaporated. Mixtures of liquid oxygen and petroleum are violently explosive. It is said that a lighted candle falling into a bucket of liquid oxygen sent G. Claude to the hospital “in a very pitiable condition.” Lamp-black soaked in liquid oxygen burns slowly when ignited, but explodes violently when detonated by a fulminate primer.

The great chemical activity of oxygen is well typified by Priestley’s quaint observation, indicated on page 330. A glowing splint of wood (“cedar splints”) when plunged into oxygen bursts into flame, the carbon of the wood being oxidized to carbon dioxide ( $\text{CO}_2$ ). The inflammation of a glowing splint is often used as a test for oxygen. A mixture of air and oxygen containing less than 28-29 per cent of oxygen does not reignite a glowing splint. Oxygen combines directly with most other elements, particularly at elevated temperatures, forming **oxides**. Iodine, bromine, fluorine, gold, platinum, and argon and its companions do not combine directly with oxygen; but oxygen combines indirectly with all elements excepting the Inert Gases. If the metals be arranged in the order of their avidity or readiness to combine with oxygen, caesium, potassium, and sodium will be found at one end of the series, while platinum and the Inert Gases will be found at the other end.

The direct combination of oxygen with some of the elements can be

illustrated by placing small dry pieces of carbon, sulphur, phosphorus in deflagrating spoons, heating them until combustion begins, and then plunging each into a jar of oxygen. The glowing piece of **charcoal** burns very brightly and forms a gaseous oxide—carbon dioxide,  $\text{CO}_2$ . **Sulphur** burns with a lavender-blue flame, forming gaseous sulphur dioxide— $\text{SO}_2$ —which has the peculiar odour characteristic of burning sulphur. **Phosphorus** burns in oxygen vigorously and brilliantly, forming a white cloud of phosphorus pentoxide— $\text{P}_2\text{O}_5$ . The phosphorus pentoxide dissolves in cold water, forming metaphosphoric acid,  $\text{HPO}_3$ . These reactions will be studied in more detail when the elements in question are treated individually.

To show the combustion of **iron** in oxygen gas, tie a tuft of “steel wool” to the end of a stout iron wire by means of a piece of steel wire. Heat the end of the wool in a Bunsen’s flame until incipient combustion begins, and quickly plunge it into a jar of oxygen on the bottom of which a layer of water, sand, or asbestos paper has been placed. The iron burns with dazzling scintillations, the product of the reaction—iron oxide—falls to the bottom of the jar in fused globules. When cold, the oxide of iron resembles a blacksmith’s hammer scale. It is called black or magnetic oxide of iron (ferrosic oxide)— $\text{Fe}_3\text{O}_4$ . The reaction is usually written:



The subject of oxidation and combustion will be considered later (pages 345, 411).

#### § 4 Formula and Atomic Weight of Oxygen

As mentioned in Chapter 7 (page 103), the atomic weight of oxygen at 16.000 is taken as the International Standard for chemical atomic weights. The physical standard is that of the isotope of oxygen of mass 16, and since there are, in ordinary oxygen, traces of two other isotopes (see § 5 below) the two standards differ slightly—in fact, in the ratio of 1 : 1.000275.

The formula of oxygen is taken to be  $\text{O}_2$ . The evidence for this is of the same kind as led to  $\text{H}_2$  as the formula of hydrogen (see pages 82 and 294). Experiment shows that from one volume of oxygen there are formed two volumes of steam, or of carbon monoxide or of nitric oxide. From which it follows that one molecule of oxygen must contain *at least* two atoms. That it does not contain more than two atoms is shown by the fact that the ratio of its specific heats is 1.4 (cf. page 84).

#### § 5 Isotopes of Oxygen

Before 1929 it was believed that oxygen was a “pure” element, that is, consisting of atoms of one mass only. In that year, however, it was shown by Giauque and Johnston that the analysis of the spectra

of atmospheric absorption bands indicated the existence of an isotope of mass 18, and a little later a still rarer isotope of mass 17 was reported. The ratio of the abundance of these isotopes has proved difficult to determine, but the figures at present accepted are 0.20 per cent of the isotope of mass 18, and 0.037 per cent of that of mass 17.

Attempts have been made to concentrate the heavier isotopes of oxygen by the electrolysis of aqueous solutions, and by the fractionation of liquid oxygen, but so far the effects observed have been very slight. It is also proposed to attempt it by diffusion.

The bearing of the discovery of isotopes of oxygen and the discovery of heavy hydrogen on the evaluation of atomic weights, has already been discussed (pages 146, 296).

### § 6 Uses of Oxygen

Oxygen is used in medical practice as already mentioned (page 335), and in cases of artificial respiration it is sometimes employed mixed with carbon dioxide or with helium.

Oxygen is used in conjunction with hydrogen for the oxy-hydrogen flame (q.v.), and with acetylene for the oxy-acetylene flame used in welding. Thick steel plates can be cut with ease by playing a fine stream of oxygen on the red-hot metal. Advantages are claimed for enriching with oxygen the air-blast of a blast furnace. Oxygen is used in bleaching, in the oxidation and thickening of oils to be used in making varnishes, linoleum, etc.

Liquid air, or rather liquid air enriched with oxygen, furnishes the explosive *oxylignite* when mixed with charcoal; 3 cm. cartridges charged with one part carbon, one part petroleum, and eight parts of liquid oxygen were tried experimentally when cutting the Simplon Tunnel. The cartridges are exploded by an electric fuse and a mercury fulminate cap. The chief objection is that the cartridges must be used within three minutes after charging, or the oxygen will evaporate. This objection might be an advantage under some circumstances, since a misfired shot is harmless in a short time.

### § 7 Oxides

The compounds of the elements with oxygen are called **oxides** and are important substances. They can be classified, broadly speaking, into six main groups. These are:

- (i) Neutral oxides.
- (ii) Acidic oxides.
- (iii) Basic oxides.
- (iv) Amphoteric oxides.
- (v) Peroxides.
- (vi) Mixed or compound oxides.

### Neutral Oxides

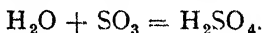
These are oxides which do not exhibit any tendency to form salts either with acids or bases; nitrous oxide is an example.

### Acidic Oxides

These are oxides which react with bases to form salts. An instance of such an oxide is carbon dioxide, which will react, for example, with sodium hydroxide solution, forming sodium carbonate:



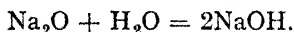
It often happens that such oxides will react with water, forming acids. A good example is furnished by sulphur trioxide which combines readily with water, forming sulphuric acid, a reaction which is employed for the manufacture of this acid (page 501):



Oxides such as sulphur trioxide and phosphorus pentoxide, which form acids with water, are also called **anhydrides** or "acid anhydrides," from the Greek  $\alpha$ , without;  $\text{ὑδωρ}$  (*hydor*), water. Thus  $\text{SO}_2$  is not only called sulphur dioxide, but also sulphurous anhydride; and  $\text{P}_2\text{O}_5$  is not only phosphorus pentoxide, but phosphoric anhydride. An anhydride can be regarded as the residue left when the elements of water are removed from an oxy-acid. Thus sulphuric acid, less water, gives sulphuric anhydride,  $\text{SO}_3$ , also called sulphur trioxide; sulphurous acid, less water, gives sulphurous anhydride,  $\text{SO}_2$ . Other important acid anhydrides, or acid-oxides, are silica, carbon dioxide, nitrogen trioxide and pentoxide, and the oxides of the halogens. From this it appears that the oxides of non-metals are usually acidic oxides.

### Basic Oxides

Many oxides are found to react with acids to form salts and water. Such oxides are called basic oxides, and, if they are soluble in water, that is, if they form soluble hydroxides, they are known as **alkalis**. Sodium monoxide, which combines with water to form sodium hydroxide, in solution if excess of water be used, is an example of this:



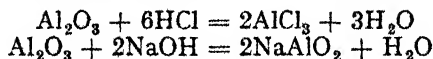
Important examples of basic oxides are the oxides of calcium, copper and iron. Basic oxides are always the oxides of metals.

### Amphoteric Oxides

It is found that there are a number of oxides which can behave either as acidic or as basic oxides according to circumstances. Thus, aluminium oxide will react with hydrochloric acid, forming a solution of aluminium chloride, thus behaving as a basic oxide when in acid



solutions; it will also react with concentrated sodium hydroxide solution, forming sodium aluminate:



thus behaving as an acidic oxide when in alkaline solutions. Such oxides are called amphoteric oxides. Other examples are the oxides of zinc, arsenic, and antimony, stannous oxide and lead monoxide.

### Peroxides

A true peroxide is an oxide which, when treated with dilute acids, yields hydrogen peroxide. An example of such an oxide is barium dioxide:

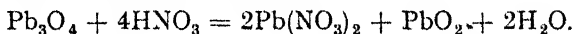


Peroxides may be thus thought of as salts of hydrogen peroxide, which in turn is then considered to be a weak acid.

The term peroxide is often loosely applied to higher oxides such as  $\text{PbO}_2$  and  $\text{MnO}_2$ . These, however, do not yield hydrogen peroxide with dilute acids, but give the salts of the lower oxides and free oxygen (or if hydrochloric acid is used, chlorine). They probably differ, therefore, in structure from true peroxides. In order to distinguish between these two kinds it has been proposed to call those which yield hydrogen peroxide **superoxides** or true peroxides, and those which give oxygen **polyoxides**.

### Compound Oxides

These are oxides which behave as though they are compounds of two oxides; though it is not certain that they are all compounds of this sort. A familiar example is red lead,  $\text{Pb}_3\text{O}_4$ , which behaves like a compound of  $2\text{PbO}$  and  $\text{PbO}_2$ , for, when treated with nitric acid, lead nitrate is formed and lead dioxide is deposited:



Red lead here seems to be a lead salt of the weak acid corresponding to  $\text{PbO}_2$ . Other examples of this type of oxide are ferrosic oxide (triferrous tetroxide),  $\text{Fe}_3\text{O}_4$ , and the similar oxide of manganese,  $\text{Mn}_3\text{O}_4$ .

The oxides of the elements are among the most important of their compounds, and their properties are of importance in relation to the classification of the elements (cf. Chapter 9). Thus, boron, carbon, nitrogen, phosphorus, sulphur, selenium, tellurium, chlorine, bromine and iodine form *only acidic oxides*; whilst sodium, potassium, calcium, strontium, barium, copper, silver, cadmium, mercury, cobalt, nickel and platinum have oxides with *basic* properties only. Again, zinc, aluminium, tin, lead and gold yield *amphoteric oxides*.

### § 8 Preparation of Oxides

The methods of preparing the oxides of the several elements are described in the chapters on the elements themselves, but the subject is one of sufficient importance to warrant collecting together here, in summary form, the principal methods available. These are:

Burning element in air (or oxygen), e.g.,  $\text{CO}_2$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{MgO}$ ; burning element in steam, e.g.,  $\text{MgO}$ ; action of steam on element at red heat, e.g.,  $\text{Fe}_3\text{O}_4$ ,  $\text{CO}$ ; heating in air, sometimes under specific conditions, e.g.,  $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ ; decomposition of hydroxide by heat, e.g.,  $\text{CuO}$ ; decomposition of carbonate by heat, e.g.,  $\text{CaO}$ ; decomposition of nitrate by heat, e.g.,  $\text{CuO}$ ,  $\text{ZnO}$ ; oxidation by nitric acid, e.g.,  $\text{SnO}_2$ ; reduction of higher oxide, e.g.,  $\text{CO}$ ; decomposition of compound oxide, e.g.,  $\text{PbO}_2$  from  $\text{Pb}_3\text{O}_4$ .

### § 9 Acids, Bases and Salts

The classification of oxides given in § 7 depends to a large extent upon their behaviour towards acids and bases. Some detailed consideration of what is meant by these terms is therefore necessary.

The early chemists appear to have learned gradually to arrange certain substances into two groups according as these substances possessed certain qualities in common with vinegar or with wood ashes. The former were called **acids** (from the Latin, *acidus*, sour); and the latter **alkalis** (from the Arabian *alkali*, ashes of a plant), because the alkalis were generally obtained by calcining various materials and reducing them to ashes. Towards the end of the seventeenth century, Robert Boyle summarized the properties of acids as substances which (1) have a sour taste; (2) dissolve many substances (corrosive); (3) precipitate sulphur from alkaline solutions of sulphur; (4) change many vegetable blue colours (e.g., blue litmus) red; and (5) lose their acid characteristics when brought into contact with the alkalis. The alkalis were considered to be substances which (1) possessed detergent and soapy properties; (2) dissolved oils and sulphur; (3) restored vegetable colours reddened by acids; and (4) had the power of reacting with acids to produce indifferent substances.

The properties of acids and alkalis were thus opposed to one another; for, when mixed together, the one neutralized the other. **Salts** were considered to be products of the interaction of acids and alkalis. It was soon found that some substances with alkaline qualities did not melt nor change when heated, and were almost insoluble in water—these substances were called *earths*. In 1744 G. F. Rouelle employed the word *base* to include the earths, alkalis, metallic oxides ("calces"), and all substances which produce salts by reacting with the acids.

#### Acids

In his study of the properties of oxygen, Lavoisier noticed that when certain elements were burnt in oxygen, the resulting oxide forms an

acid with water—e.g., carbon, sulphur, and phosphorus. Hence Lavoisier concluded (1777) that “oxygen is an element common to all acids, and the presence of oxygen constitutes or produces their acidity.” Lavoisier considered oxygen to be the essential constituent of all acids. The very name *oxygen*, given to this element, was derived from Greek words signifying “the generative principle of acids” *ὄξυς* (*oxus*), sour, and *γεννάω* (*gennao*), I produce.

With increasing knowledge, it was found that Lavoisier's oxygen theory of acids led to confusion and error, and it was gradually abandoned by chemists when it was recognized that:

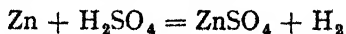
1. *Some oxides form alkalis, not acids, with water.*—E.g., sodium, potassium, and calcium oxides.

2. *Some acids do not contain oxygen.*—C. L. Berthollet showed, in 1787, that hydrocyanic (prussic) acid is a compound of carbon, nitrogen, and hydrogen, but contains no oxygen; and he also came to a similar conclusion with regard to hydrogen sulphide. But for some time Lavoisier's reputation had more weight than Berthollet's facts. In 1810–11 Humphry Davy proved that hydrochloric acid is a compound of hydrogen and chlorine, and that no oxygen could be detected in the compound. In 1813 Davy also proved that hydriodic acid contained hydrogen and iodine, but no oxygen. Hence, added Davy, “acidity is not connected with the presence of any one element.”

In 1815 Davy suggested the possibility that hydrogen, not oxygen, gives the acid characters to the acids; but he did not rush to the other extreme and say that all hydrogen compounds are necessarily acids. There is no one property which we can use as an absolute criterion or decisive test of acidity. In a crude sort of way, it can be said that *acids usually have a sour taste, are usually corrosive, reddens the blue colour of vegetable substances (e.g., litmus), and contain hydrogen, part or all of which can be replaced when the acid is treated with a metal, metallic oxide, hydroxide, or carbonate.* Acids are known with a sweet taste, and which are not corrosive. Alum does not contain replaceable hydrogen, and it would not therefore be classed as an acid, although it is sour, corrosive, and colours blue litmus red. But we are far from a satisfactory definition of acids, although, as has been said in Chapter 18, a very fair definition can be framed in terms of the Ionic Theory.

## Salts

In modern chemistry the word **salt** is a descriptive term applied to a distinct family of substances and not to any particular individual. In the kitchen, “salt” is colloquially applied to one specific individual, sodium chloride. A salt is produced by replacing all or part of the hydrogen of an acid by a metal or basic radical. For instance, zinc displaces the hydrogen of sulphuric acid:



forming zinc sulphate, as indicated on page 288. Hence C. Gerhardt (1843) defined acids to be "salts of hydrogen."

In **normal salts** all the displaceable hydrogen of the acid is replaced by the base. For instance, sodium sulphate— $\text{Na}_2\text{SO}_4$ —is a normal salt because all the replaceable hydrogen of sulphuric acid is displaced by sodium. In **acid salts** only part of the replaceable hydrogen has been displaced by a base, and the salt still contains replaceable hydrogen. For instance, acid sodium sulphate— $\text{NaHSO}_4$ —contains half the replaceable hydrogen of sulphuric acid, and half as many equivalents of sodium as normal sodium sulphate. If an acid contains two or more replaceable hydrogen atoms, it does not follow that all need be displaced by the same element. Thus, for example:

$\text{H}_2\text{SO}_4$ —sulphuric acid.

$\text{NaHSO}_4$ —sodium hydrogen sulphate.

$\text{Na}_2\text{SO}_4$ —sodium sulphate.

$\text{NaKSO}_4$ —sodium potassium sulphate.

Sometimes the term "hydrogen" is used in place of "acid" for the acid salts, and sometimes the prefix "bi-" is appended to the term for the acid in the salt. Thus "acid sodium sulphate" is also called, as above, "sodium hydrogen sulphate," "sodium bisulphate," as well as "mono-sodium sulphate," etc. The normal salts are sometimes called "neutral salts" in the sense that all the hydrogen has been "neutralized" or displaced from the acid. These salts, however, are not necessarily neutral to litmus—thus normal zinc or copper sulphates react towards litmus as if they were acids; borax, sodium nitrite, and normal sodium carbonate react as if they were alkalis.

It is sometimes necessary to use the prefixes mono-, di-, tri-, . . . to discriminate between the different salts of one acid. Thus with phosphoric acid:

$\text{H}_3\text{PO}_4$ —phosphoric acid.

$\text{NaH}_2\text{PO}_4$ —sodium dihydrogen phosphate.

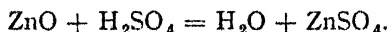
$\text{Na}_2\text{HPO}_4$ —disodium hydrogen phosphate.

$\text{Na}_3\text{PO}_4$ —normal, or tri-sodium phosphate.

It would be a mistake to assume that all the hydrogen of an acid is necessarily replaceable by a base. Thus, so far as we know, hypophosphorous acid— $\text{H}_3\text{PO}_2$ —has only one of its three hydrogen atoms replaceable by a metal. No one has ever prepared  $\text{Na}_2\text{HPO}_2$ , or  $\text{Na}_3\text{PO}_2$ . Similarly, acetic acid— $\text{C}_2\text{H}_4\text{O}_2$  or  $\text{CH}_3\cdot\text{CO}_2\text{H}$ —has only one hydrogen atom replaceable in this way. **The number of atoms of hydrogen in one molecule of an acid which are replaceable by a metal, or a radical, is termed the basicity of the acid.** Thus hydrochloric acid— $\text{HCl}$ —is monobasic because each molecule of hydrochloric acid contains one replaceable hydrogen atom; sulphuric acid— $\text{H}_2\text{SO}_4$ —is dibasic; phosphoric acid— $\text{H}_3\text{PO}_4$ —is tribasic; and orthosilicic acid— $\text{H}_4\text{SiO}_4$ —is tetrabasic. Hypophosphorous acid— $\text{H}_3\text{PO}_2$ —and acetic acid— $\text{C}_2\text{H}_4\text{O}_2$ —are monobasic.

### Bases

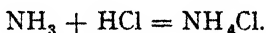
A base—Greek *βάσις* (*basis*), a base—is a substance which reacts with an acid to produce a salt and water. For instance, zinc oxide reacts with sulphuric acid to produce zinc sulphate and water:



Sodium hydroxide reacts with sulphuric acid to produce sodium sulphate and water:



The bases include the oxides and the hydroxides of the metals, and certain groups of elements equivalent to a metal. For convenience, certain groups of elements like ammonia— $\text{NH}_3$ , hydroxylamine— $\text{NH}_2\text{OH}$ , hydrogen phosphide— $\text{PH}_3$ , etc., are called bases, although they form salts by direct addition or combination without the separation of water. Thus ammonia and hydrogen chloride form ammonium chloride:

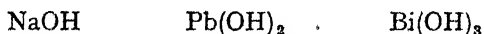


This definition is not entirely satisfactory because it depends upon the definition of an acid, which, as stated on page 341, is not easily framed unequivocally; but it works fairly well on the whole; and the difficulties are, to a considerable extent, overcome by the application of the Ionic Theory (see § 10, below).

The term base was originally intended to express the idea that the metal or metal oxide was the more important constituent, the foundation or base, so to speak, of a salt. This idea was dropped when it was recognized that the acidic constituent of a salt is just as important as the basic constituent.

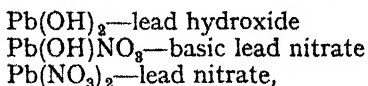
It is necessary to avoid any confusion between the terms "alkali" and base, for they are not synonymous. Most alkalis are bases but not every base is an alkali. The distinction between the two has already been referred to (page 340); what it amounts to is that the soluble bases are alkalis.

The hydroxides of sodium, lead and bismuth have a composition represented by the formulae:



and inspection of these reveals an analogy with the formulae of acids such as hydrochloric, sulphuric and phosphoric in that the hydroxides contain one, two and three hydroxyl groups respectively, whereas the acids have one, two and three hydrogen atoms respectively. It is natural, therefore, to inquire if salts can be formed by replacement of one or more of these hydroxyl groups by acids, just as the hydrogen of phosphoric or sulphuric acids can be replaced one by one by bases. If this is so, it would be anticipated that **basic salts** should exist, corresponding to the acid salts already discussed.

Such salts do, in fact, exist so that there can be obtained:



a series corresponding, *mutatis mutandis*, to that given on page 342. A corresponding nomenclature is also employed—a hydroxide such as lead hydroxide is termed a di-acid base, and in general, **the number of hydroxyl groups replaceable by acid which a base contains is termed the acidity of the base.**

Sometimes two different salts react together to form either a **double salt** or a **complex salt**. A double salt, in solution, shows the reactions of all the ions originally present, whereas in a complex salt a new ion is formed from the ions of the mixed salts and so the reactions of some of the ions originally present are no longer observable. An example of a double salt is an alum such as potash alum which, in solution, gives the reactions of potassium, aluminium and sulphate. A well-known complex salt is potassium ferrocyanide which, although it can be made by the combination of potassium cyanide and ferrous cyanide, does not give the reactions of ferrous iron; the iron is now part of a complex ferrocyanide ion  $[\text{Fe}(\text{CN})_6]^{4-}$  which is very stable in solution.

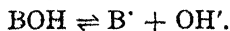
### § 10 Acids, Bases and Salts according to the Ionic Theory

In Chapter 15 it was stated that certain chemical compounds are marked off from others in that their solutions in water are capable of conducting an electric current, and also exhibit other characteristic properties. In Chapter 11 these were distinguished also as being what is termed electrovalent compounds. An examination of compounds exhibiting this behaviour shows that they are all substances which, apart from these characteristics, would be included in the groups of substances which are called acids, bases or salts. So far no attempt has been made in the present chapter to define these substances in terms of the theory—the theory of electrolytic dissociation or the Ionic Theory—which is believed to explain these phenomena.

According to the Ionic Theory, an acid is an electrovalent substance which in solution in water yields hydrogen ions as the only positive ions. This is represented by the equation:



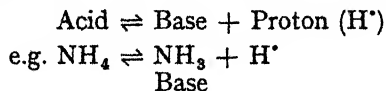
Similarly, an alkali or a base may be defined as a substance which will yield hydroxyl ions as the only negative ions; which may be expressed by the equation:



Lowry and Brønsted have defined acids and bases somewhat differ-

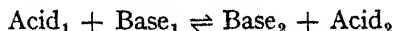
ently as substances (whether molecules, radicals or ions) which give up (or accept) protons.

These definitions obviate the difficulty that many compounds (such as oxides, sulphides, etc.) exhibit basic properties; they also remove the limitations of neutralization processes to those in which water is the solvent. The Lowry and Brønsted definitions lead to the expression



a concept of importance where reactions in liquid ammonia are concerned.

Molecules and ions which, according to these definitions, are inherently acids or bases exhibit these properties only when, with an acid, a proton acceptor is available or, with a base, a proton donor is present. Acid-base relations may then be written



Water may then behave either as an acid or a base and, as a solvent, will compete for protons with other molecules or ions. According to the Lowry and Brønsted definitions salts are regarded as aggregates of positive and negative ions. This concept also accounts for the phenomena of neutralization and solvolysis in non-aqueous solvents.

## § 11 Oxidation and Reduction

The terms oxidation and reduction have been used several times already, and now call for more extended treatment.

The conversion of an element into its oxide by direct combination with oxygen is the simplest case of oxidation. For example, when copper is heated in air it is *oxidized* on the surface to copper oxide. Similarly, any process which will convert an element into its oxide is an oxidation. An analogous process may involve the combination of a compound already containing some oxygen with still more oxygen, as for example when barium oxide is heated in air to a suitable temperature and thereby converted into barium dioxide (page 334).

This again is clearly an oxidation. Oxidation, in the simplest case, is thus a process which adds oxygen to an element or compound.

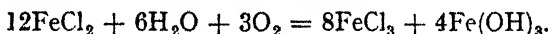
The reverse of this process, that is, the removal of oxygen from a compound containing it, is known as reduction. Thus, for example, when copper oxide is converted into copper by passing hydrogen over the heated oxide, the copper oxide is said to be *reduced* to copper. This is the original idea underlying the terms oxidation and reduction, and is the simplest use.

It soon became evident, however, that the process of removing hydrogen from a compound containing that element involves something closely akin to oxidation as indicated above, and, similarly, the

addition of hydrogen closely resembles reduction as previously understood. The same reagents will often bring about both addition of oxygen and removal of hydrogen, or vice versa, and the changes brought about in the state of combination of an element are similar. Hence, the idea of oxidation and reduction was extended to cover these cases.

As chemistry developed, it was realized that some processes which do not directly involve hydrogen and oxygen at all are in principle so closely related to oxidation and reduction, as understood when referred simply to changes in the oxygen or hydrogen content of a compound, that the idea has been still further extended.

For example, ferrous oxide,  $\text{FeO}$ , is a base which gives rise to a series of salts called the ferrous salts. Ferrous oxide can be oxidized, for example, by the oxygen of the air, to ferric oxide,  $\text{Fe}_2\text{O}_3$ . Ferric oxide in its turn is a base which with acids forms ferric salts. Ferrous and ferric salts thus stand in the same relationship to each other as ferrous and ferric oxides. Now a solution of a soluble ferrous salt, on exposure to air, will slowly turn to the ferric salt—clearly oxidation has occurred. For example, ferrous chloride is converted partly into ferric chloride and partly into ferric hydroxide:



But ferrous chloride can be converted very simply into ferric chloride by the action of chlorine:



which must be reckoned to be an oxidation since it is agreed that the conversion of ferrous chloride into ferric chloride is an oxidation. But no oxygen has taken part in the process. Hence the term oxidation must be extended to cover this process.

Conversely, reduction must also be similarly extended. Similar reasoning to the above indicates that the conversion of mercuric chloride,  $\text{HgCl}_2$ , into mercurous chloride,  $\text{Hg}_2\text{Cl}_2$ , is a process of reduction. This can be brought about by means of stannous chloride, for example, without the intervention of hydrogen at all:



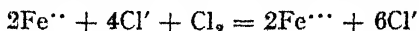
This last example illustrates one very important fact. Mercuric chloride is reduced to mercurous chloride in this reaction, but the stannous chloride by means of which this result is brought about is changed into stannic chloride; in other words, it has been oxidized. In general, oxidation and reduction are reciprocal processes; one substance is oxidized while the other is reduced.

It is thus necessary to extend the definition of oxidation and reduction so as to include all these types of reaction. The term **oxidation** is applied to **any process which involves the passage of a compound representing a lower stage of combination with oxygen to a substance**

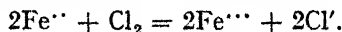


equivalent to a higher stage of combination with oxygen, by the addition of oxygen or of an electronegative atom or radical, or by the removal of hydrogen or an electropositive atom or radical. Reduction is the converse of oxidation.

In terms of the Ionic Theory, oxidation and reduction are seen to involve merely the transference of electrical charges. Thus the conversion of ferrous chloride into ferric chloride written in terms of ions becomes:

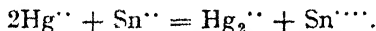


or eliminating the terms common to both sides of this equation:



That is to say, the ferrous ion loses one negative charge (or electron) and thus becomes a ferric ion, while each atom of the chlorine molecule gains one negative charge (or electron).

The reduction of mercuric chloride can be represented in terms of ions by the equation:



Reduction is thus a matter of making smaller the number of positive charges on an ion, and oxidation of increasing them.

An oxidizing agent is a substance which can bring about oxidation as defined above, and a reducing agent conversely.

Among the **available oxidizing agents** are: oxygen, ozone, the peroxides, and the higher oxides as well as the unstable basic oxides of silver, gold, etc.; the oxy-acids (nitric, nitrous, chromic, chloric, and the other oxy-acids of the halogens) and their salts; the halogens (chlorine, bromine, iodine); permanganic acid and its salts; potassium ferricyanide, etc.

Among the **available reducing agents or deoxidizers** are: hydrogen, unstable hydrides (hydrogen sulphide, hydrogen iodide, phosphine, arsine, stibine, etc.); carbon, carbon monoxide, sulphur dioxide, and the sulphites; phosphorous acid and the phosphites; hypophosphorous acid and the hypophosphites; potassium cyanide; potassium formate; ferrous, stannous, and chromous salts; the metals sodium, potassium, magnesium, aluminium, etc.

## § 12 Ozone

### Historical

Van Marum observed the peculiar smell (now known to be that of ozone) when an electrical discharge takes place in air; and this was attributed to a new gas, and given the name ozone (from the Greek *ὄζω*, *ozo*, I smell) by Schönbein in 1840.

### Formation

Ozone is produced by the action of the ultra-violet rays and radium radiations on oxygen. It is said to be formed by the violent mechanical

disturbance of air as when grinding wheels are being tested for bursting speed; but the effect may here be due to the electrification of the air. Ozone can generally be detected in the oxygen gas obtained during the electrolysis of acidulated water. By the electrolysis of sulphuric acid (between 1.075 and 1.1 specific gravity), with an anode made by embedding platinum foil in glass and grinding away the edge so that a line of platinum, 0.1 mm. broad, is exposed, oxygen containing 17 to 23 per cent of ozone has been obtained. The yield increases with increasing current density.

The oxygen liberated by many reactions also contains ozone. For instance, manganese dioxide and sulphuric acid; barium dioxide and sulphuric acid; potassium permanganate and sulphuric acid, persulphuric acid, persulphates, etc. Purified potassium chlorate gives oxygen free from ozone, but if traces of some indifferent substances be present, ozone may be formed. When fluorine decomposes water forming hydrogen fluoride and oxygen, from 13 to 14 per cent of the "oxygen gas" is ozone.

Ozone is formed during the slow oxidation of many substances. Ozone can be detected in the atmosphere of a flask containing a couple of sticks of clean phosphorus.

Ozone is also said to be formed when turpentine, several hydrocarbons, coal tar, and many essential oils are oxidized. Ozone is said to be formed during the combustion of ether as well as during the combustion of hydrogen compounds generally.

The formation of ozone by the evaporation of water or dew is said to account for the bleaching of linen spread on lawns.

Much atmospheric ozone seems to be formed by the action of solar ultra-violet light in the upper regions of the atmosphere. Ozone is here present in relatively greater proportions; thus, on the Alps at an altitude of 20 kilometres the air had 5 parts of ozone per million (volumes); and at an altitude of 2.1 kilometres, half this proportion. Electrical discharges in the atmosphere also produce ozone. Homer in several passages referred to the odour which attended the "thunderbolts" or flashes of lightning.

### Preparation of Ozone

The most usual method of making ozone, or rather of preparing ozonized air and ozonized oxygen, is to expose dry air or oxygen to a silent discharge of electricity. Quite a number of instruments are available. That illustrated in Fig. 21.3 is virtually the one devised by W. von Siemens (1858). It consists of two concentric tubes. The inner tube is coated on its inner surface with tinfoil in metallic contact with the terminal *A*; and the outer tube is coated on its outer surface with tinfoil in metallic contact with the terminal *B*. The two terminals are connected with an induction coil. A slow stream of dry oxygen is led through the annular space between the concentric tubes, and is there exposed to the action of a silent discharge of electricity. The

gas issuing from the ozonizer is charged with 3 to 8 per cent of ozone. In *Brodie's or Berthelot's ozone tube* the tinfoil coatings are replaced by sulphuric acid (Fig. 21.3). If air be used in place of oxygen, some nitrogen oxides are said to be formed at the same time. The presence of moisture reduces the yield of ozone,\* although no difference has been detected in the amount of decomposition of the dry and moist gas when heated for some time at 100°.

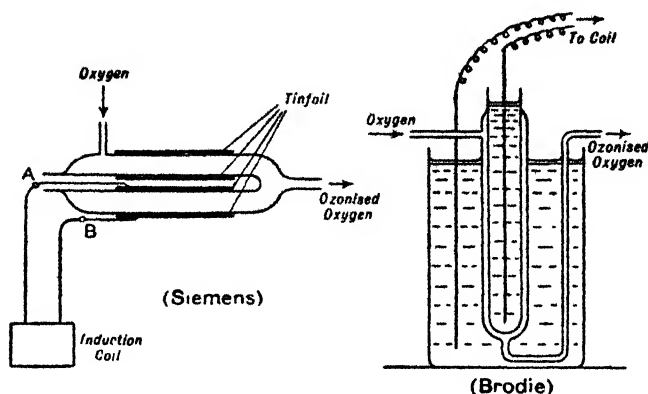


FIG. 21.3. Ozonizers

When required to be produced commercially, ozone is also obtained by means of a silent discharge, but a modified type of apparatus is employed such as that shown in Fig. 21.4.

### §13 Properties of Ozone

Ozonized air has a strong unpleasant smell. The smell reminds some people of sulphur dioxide, others of garlic, and others of chlorine. If air highly charged with ozone be breathed for any length of time, it produces headache; but in minute quantities the odour is pleasing and refreshing. Ozone is slightly soluble in water—100 volumes of water at ordinary temperatures and pressure dissolve about one volume of ozone—and the water smells of the ozone and exhibits many of the properties of ozone. The water slowly reacts with the ozone.

Ozone is dissolved by essential oils such as turpentine, cinnamon oil, etc. This is because these oils contain what in organic chemistry are known as unsaturated compounds, that is, the molecules of these compounds contain one or more pairs of carbon atoms united by a "double bond." Such compounds readily form addition products with bromine or with ozone.

Unlike oxygen, ozone liberates iodine from neutral potassium

\* Ozone is decomposed by cork and indiarubber. In consequence, these materials should not be used for any part of the ozonizer in contact with the gas.

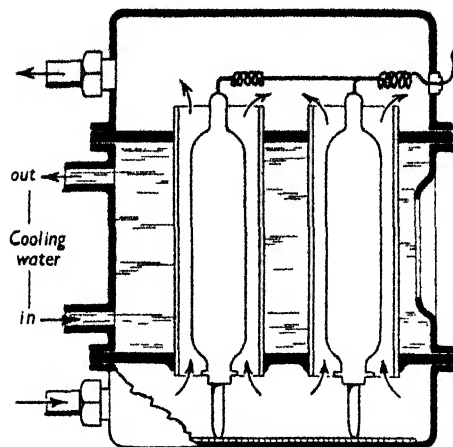
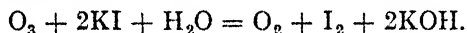
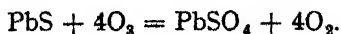


FIG. 214.—Commercial Ozonizer  
(Siemens and Halske)  
(Modified from Partington, "General and  
Inorganic Chemistry," Macmillan)

iodide. This can be shown by dipping paper in a solution of potassium iodide and holding it at the exit tube of the ozonizer. The paper turns brown owing to the liberation of iodine. If a little starch be mixed with the potassium iodide, the paper will appear blue. The reaction is usually represented:



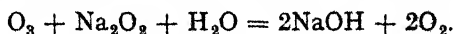
Ozone is a very powerful oxidizing agent. Organic matter—cork, rubber, etc.—is rapidly corroded by ozone. Paper coloured by a solution of indigo sulphate or a solution of litmus is bleached. If a globule of mercury is placed in a small flask and ozonized air passed in, the mercury loses its lustre and spreads a film over the walls of the flask. Ozone is said to cause mercury to "tail." The globule of mercury is restored when the film is shaken up with water. If a piece of silver foil, cleaned with silver sand, be heated in a bunsen burner for a moment, and while still warm held in a stream of ozonized air, the silver is blackened, owing, it is said, to the formation of silver peroxide. Silver perfectly free from the oxide does not show the reaction at ordinary temperatures unless the metal be contaminated with some substance like oxide of cobalt, nickel, etc., which acts as a catalytic agent. A trace of oxide is supposed to be formed when the silver is heated in the bunsen burner. The reaction is characteristic of ozone, but it is not very sensitive. Ozone converts dark brown coloured lead sulphide into white coloured lead sulphate:



Many other sulphides—copper, antimony, zinc, cadmium—behave in a similar manner. Nickel and cobalt sulphides form peroxides and sulphuric acid. A solution of manganous sulphate used as an invisible ink is browned by exposure to ozone.

Ozone decomposes in the presence of finely divided platinum, lead dioxide, manganese dioxide, silver and copper oxides. The ozone is converted into ordinary oxygen without decomposing the oxides. Hence the reactions are grouped among catalytic reactions.

When ozone is brought into contact with sodium peroxide, the two substances mutually decompose and oxygen is liberated:



Ozone seems to be fairly stable at ordinary temperatures, although it gradually decomposes on standing. It also appears to be fairly stable at high temperatures, while at intermediate temperatures it is unstable.

By passing ozonized oxygen through a tube cooled by immersion in boiling liquid oxygen, a solution of ozone in liquid oxygen is obtained. By reducing the pressure the liquid boils and separates finally into two layers: an upper deep blue one, which is a solution of ozone in liquid oxygen, and a lower violet one, which is oxygen dissolved in liquid ozone. If the oxygen be pumped off the ozone-rich layer and the residue fractionally distilled, very dark blue pure liquid ozone is obtained from which, by careful evaporation, pure gaseous ozone results (Riesenfeld and Schwab, 1922). The liquid is said to be explosive.

#### § 14 Formula and Structure of Ozone

The determination of the formula of ozone presented many difficulties, so long as pure ozone could not be obtained.

The question whether ozone is elementary in nature or not caused considerable controversy, and for some time it was uncertain whether it should be regarded as an allotropic form of oxygen or as an "oxidized" form of water. It was proved in 1860, by Andrews and Tait, that ozone is a condensed form of oxygen. This they did by exposing pure, dry oxygen to a silent discharge in a sealed tube, attached to a manometer, when a contraction in volume was observed. On heating the ozonized oxygen so formed, expansion to the original volume took place. Further, when a small sealed tube containing potassium iodide was placed in the larger tube of oxygen and broken after a silent discharge had been passed and a contraction in volume had occurred, iodine was liberated without change of volume. The residual gas, on heating, now showed no increase in volume. Hence, ozone is a form of oxygen. This conclusion was also confirmed by Soret in 1863. He took thoroughly dried ozone, decomposed it by heating, and showed that no trace of any compound of hydrogen (such as water) could be detected.

These experiments served to show that ozone contains only oxygen,

but do not indicate how many atoms there are in a molecule of ozone. This was first demonstrated by Soret in 1866.

He took advantage of the fact that essential oils absorb ozone without decomposition. He confined similar samples of ozonized oxygen in 250 c.c. flasks over water. In one the ozone was absorbed by means of turpentine, while the other flask was heated, thus decomposing the ozone. The mean of his experiments gave a contraction of 6.26 c.c. in the first flask and an expansion of 3.26 c.c. in the second (approximately half the former figure). Hence he inferred that **three volumes of oxygen produce two volumes of ozone**.

Now if the formula of ozone is  $O_n$  we have, when it is decomposed:



that is to say, according to Avogadro's hypothesis, 2 volumes of ozone are formed from  $n$  volumes of oxygen. Soret's experiment showed that 3 volumes of oxygen produce 2 volumes of ozone. Therefore,  $n = 3$  and the formula for ozone is  $O_3$ .

Soret's work was rather crude, but B. Brodie (1872) repeated the experiments with cinnamon oil, turpentine, stannous chloride, in such a way that the above conclusion was the only possible interpretation of the experiments.

This formula has been confirmed by diffusion experiments carried out by Soret (1868) and by effusion by Ladenburg (1898), as mentioned on page 34. Further, Riesenfeld and Schwab determined the vapour density of pure ozone by Dumas's method, and found it to be 24, corresponding to the formula  $O_3$ .

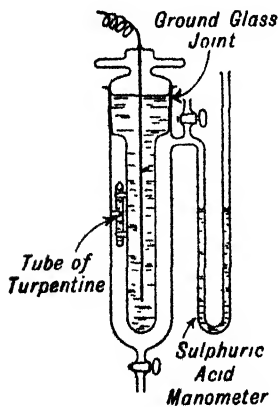


FIG. 21.5.  
Newth's Apparatus

The constitution of ozone may be demonstrated in the laboratory by means of Newth's apparatus (Fig. 21.5). It consists of two concentric tubes united by a ground glass joint. The inner tube contains dilute sulphuric acid and has two small projections fused on to it. A similar projection is fused on to the outer tube in such a way that a small sealed thin glass tube containing turpentine can be held between the projection and later broken by twisting the inner tube. A platinum wire dips into the sulphuric acid and the apparatus is immersed in a cylinder of dilute sulphuric acid (not shown in the diagram) into which is inserted another platinum wire. The annular space between the tubes is filled with dry oxygen

and the manometer is levelled. The oxygen is subjected for a short time to a silent electric discharge by connecting the platinum wires to an induction coil and the contraction caused by the formation of ozone

read from the manometer. The small tube of turpentine is now broken by twisting the inner tube and the further contraction noted. Within the limits of experimental error the second contraction is twice the first, leading to the formula  $O_3$ .

Ozone was formerly thought to have a cyclic structure:



but this is not supported by the value of its heat of formation from oxygen nor by the measured lengths of the bonds between the oxygen atoms. Pauling (1943) has suggested that it consists of a resonance hybrid between four non-linear open chain structures



### § 15 Detection and Determination of Ozone

The detection of ozone is complicated by the fact that many of the most obvious of its reactions are similar to those of other oxidizing agents.

Ozone may be detected by its action on mercury, or by its action on clean silver foil, which is blackened by ozone. It liberates iodine from potassium iodide in common with many other oxidizing agents, but may be distinguished from others, except hydrogen peroxide, in that it will not liberate iodine after passage through a hot tube.

The real difficulty arises in distinguishing ozone from hydrogen peroxide. This may be done by means of potassium permanganate solution which is decolorized by hydrogen peroxide but not by ozone. Alternatively, C. Arnold and C. Mentzel (1902) propose the use of test-papers soaked in an alcoholic solution of "tetramethyl base." These are not affected by hydrogen peroxide, but are turned violet with ozone; blue with chlorine and bromine; and bright yellow with nitric oxide. C. Engler and W. Wild (1896) state that if a mixture of ozone and hydrogen peroxide be passed through a concentrated solution of chromic acid, the hydrogen peroxide is alone decomposed, the ozone is not affected. The same investigators say that paper steeped in a concentrated aqueous solution of manganous chloride is turned brown by ozone, but not by hydrogen peroxide.

Some reactions of ozone, hydrogen peroxide, chlorine, and nitrogen peroxide are compared in Table XXIX.

The method used for the determination of ozone in air consists in passing a known volume of air through a neutral solution of potassium iodide. The liberated iodine is determined by acidifying the solution, and titrating it with a standard solution of sodium thiosulphate (page 567). A standard method for estimating ozone in, say, the atmosphere is to expose ozone test papers\* for a definite time to the air

\* Papers steeped in an emulsion of starch containing a small proportion of potassium iodide are called ozone test papers.

and compare the resulting tint with a standard scale of colours obtained with air containing known quantities of ozone. Since other oxidizing substances likely to be present in air produce a similar reaction, it is a moot question whether the large number of "ozone determinations" which have been made really represent ozone, or hydrogen peroxide, nitrogen oxides, chlorine, etc. Rather does the result of the test represent the presence of "oxidizing substances."

TABLE XXIX.—DISTINGUISHING TESTS FOR OZONE AND HYDROGEN PEROXIDE

Reagent	Ozone	Hydrogen peroxide	Chlorine	Nitrogen peroxide
KI and starch . . .	Blue	Blue	Blue	Blue
Clean silver foil . . .	Blackened	Nil	White film	No change
Mercury bead . . .	Trail on glass	Nil	White	No change
CrO <sub>3</sub> and ether . . .	Nil	Blue	Nil	Nil
Titanic acid . . .	Nil	Yellow	Nil	Nil
Tetramethyl base* . .	Violet	Nil	Blue	Yellow to brown
Benzidine . . .	Brown	No change	Red	Blue

\* Tetramethyl-di-*p*-aminophenylmethane.

### § 16 Uses of Ozone

Ozone is used for the purification of water in special cases, but is rather expensive. Its function is to oxidize the organic matter, and sterilize the water. Ozonized air is also used in ventilation, e.g., in underground railways, for bleaching oxidizing oil in the manufacture of linoleum, etc. It has also been employed as bleaching agent for wax and certain other materials.



## CHAPTER 22

### CARBON

Modern civilization is the daughter of coal, for coal is today the greatest source of energy and wealth.—G. GAMACIAN (1913).

The manufacture of coal gas for purposes of illumination is one of the most striking instances of science enlisted in the divine cause of civilization. Once a luxury or convenience, it is now almost a necessity.—ANON.

#### § 1 Unique Character of Carbon

CARBON is an element which is characterized by the enormous number of compounds which it is able to form; the number of known carbon compounds is already far in excess of the number of known compounds of all the other elements taken together, and there are no signs as yet of any limit being reached. This fact has resulted in the study of the compounds of this element being made into a separate branch of chemistry known as **Organic Chemistry**, which is thus, strictly speaking, the chemistry of the compounds of carbon.

At the same time, the properties of the element itself, and of a few of its compounds which are most closely related to those of the other elements, are properly included in any scheme of Inorganic Chemistry also.

The enormous number and variety of carbon compounds are the outcome of the fact that carbon atoms can form remarkably strong chemical linkages with each other. Thus whereas chains of atoms of other elements—for example, of sulphur—are usually very unstable, chains of carbon atoms of great length and complexity are perfectly stable. In addition, carbon also forms stable linkages with a great many other elements, and in particular with hydrogen, nitrogen, oxygen, sulphur and the halogens, and so it follows that an enormous variety of stable compounds is possible.

#### § 2 Allotropy and Varieties of Carbon

Carbon exists in more than one form, that is to say, it exhibits allotropy. Until recently, it has been usual to distinguish three allotropic forms, but it is now believed that there may be two only, viz., **diamond** and **graphite**. The third so-called form, **amorphous carbon**, is held to include the different varieties of vegetable and animal charcoals—lampblack, charcoal, soot, gas carbon, and coal. These are more or less impure forms of carbon.

Modern work has shown that these varieties probably do not differ from graphite except in purity, porosity, and in the size and shape of

the actual particles. Examination by X-ray methods has shown that all these materials are composed of aggregates of microcrystalline material; these microcrystalline particles having the same relative arrangement of carbon atoms as graphite. The peculiar properties of amorphous carbon, in so far as they differ from those of diamond or graphite, and of the different kinds of amorphous carbon, are apparently due to their relatively large surfaces in proportion to their mass or the presence of impurities, and to the different ways in which the microcrystalline particles are built up into the aggregate. The nature of the impurities present (e.g., hydrogen, oxygen or sulphur) probably plays an important part in determining this.

It is clear, however, that there are many varieties of carbon, the following being usually distinguished in addition to the two pure allotropic forms, viz., lampblack, charcoal (including wood charcoal and bone or animal charcoal), coal, coke and gas carbon.

### § 3 Lampblack and Charcoal

**Lampblack** is made by burning substances rich in carbon, such as turpentine, petroleum, tar, acetylene, in a limited supply of air so that the maximum amount of smoke is developed. The smoke is passed into large chambers in which coarse "blankets" are suspended. The "soot" collects on the blankets. Lampblack is also made from natural gas.

The lampblack falls into a hopper and is conveyed by elaborate machinery to be ground to the finest powder, sifted, and weighed into sacks. Lampblack is used for making printer's ink, stove and shoe polish, paints, and in fact nearly everything in which a black pigment or colouring matter is required. It is also employed as a filler in the manufacture of rubber tyres.

Lampblack is one of the purest varieties of amorphous carbon. The analysis of a sample of acetylene "soot" furnishes 1.4 per cent of hydrogen and 98.6 per cent of carbon.

Most of the hydrocarbon impurities can be removed by heating in a current of chlorine.

### Charcoal

There are two main varieties of charcoal—wood and bone. Wood charcoal is made by burning wood with a limited supply of air in a charcoal pit or kiln; or by heating wood in closed vessels so that air is excluded.

In outline the industrial preparation is as follows: Small logs or billets of wood are loosely piled into vertical heaps and covered with sods and turf to prevent the free access of air. There are several systems of piling the sticks—one is illustrated in Plate 15. A "shaft" is left in the middle of the pile to act as a central chimney or flue; and smaller holes are left round the bottom to admit the air. The pile so

prepared is called a "charcoal pit" or a *Meiler* (German). The wood is lighted by brushwood at the centre, and just sufficient air to allow the wood to smoulder is passed through the pile. The volatile matter escapes, and in about fifteen days the fire dies out. Between 80 and 90 per cent of the weight of the wood, on the average, is lost by combustion, and the remaining 10 to 20 per cent is wood charcoal.

Some valuable gaseous and liquid products are lost in making pit charcoal. In modern processes, the wood is heated in ovens, kilns, or retorts, sealed from the outside air. The operation may be conducted simply for charcoal without recovering the by-products, or the operation may be conducted somewhat similarly to the process used for the manufacture of coal gas. The products of the dry distillation of wood include: solid charcoal in the retort; liquids—wood tar (*Stockholm tar* from pine wood); water containing wood spirit, acetic acid, acetone and fatty oils; and gaseous wood gas containing hydrogen, carbon dioxide, carbon monoxide, methane, acetylene, etc.

### Bone or Animal Charcoal

This is made by heating bones, blood, etc., in closed retorts. The bones may or may not have been subjected to a preliminary extraction with naphtha or benzene to remove the fat—degreased bones; or with superheated steam or water to remove gelatine (glue)—degelatinized bones. The products of the distillation include: solid bone charcoal in the retort; liquids—a number of ammonium salts, bone oil, bone pitch, pyridine, etc.; and gases of various kinds. Bone charcoal contains about 10 per cent of carbon, so that it is questionable if it ought to be included with the varieties of carbon at all. However, the carbon is very finely divided and disseminated through a porous mass of about 80 per cent of calcium and magnesium phosphates, and it seems to have specially valuable qualities. Bones furnish *bone black*—sometimes called *ivory black*—the term *ivory black* is usually applied to the product obtained by digesting bone black with hydrochloric acid to remove the calcium phosphates. Blood furnishes *blood charcoal*. For the uses of bone black and animal charcoal, see below; ivory black is used as a pigment; e.g., in the manufacture of blacking.

### § 4 Properties of Amorphous Carbon

Charcoal is a black porous substance of very low *apparent* specific gravity, due to the presence of a considerable volume of air entangled in the pores.

On account of its porosity charcoal possesses a very large surface in proportion to its weight so that it exhibits what are known as *surface effects* to a high degree. All solids retain a thin film of gas upon their surfaces, and on account of its large surface area charcoal can take up large quantities of many gases.

The phenomenon is sometimes styled **adsorption**, meaning that the gas adheres in some way to the surface of the charcoal. One volume of coconut charcoal adsorbs (Hunter) at 760 mm. pressure:

	B.p. of gas	Vols. at 0°	Vols. at - 185°
Ammonia . . . .	- 33.5°	171	--
Ethylene . . . .	- 104°	75	--
Carbon dioxide . . . .	- 78.5°	68	--
Carbon monoxide . . . .	- 192°	21	190
Oxygen . . . . .	- 183°	18	230
Nitrogen . . . . .	- 195.8°	15	155
Hydrogen . . . . .	- 252.7°	17	135
Helium . . . . .	- 269°	2	15
Argon . . . . .	- 186°	12	175

The gases are evolved again on heating, but when cooled in liquid air the amount of gas adsorbed becomes very much greater. Thus a piece of charcoal which will adsorb eighteen times its volume of oxygen at 0° C., will adsorb two hundred and thirty times its own volume at the temperature of liquid air ( - 185° C.).

This property affords a means of producing high vacua, and also of separating gases which are not readily adsorbed (helium, neon, page 590) from those which are readily adsorbed (air, etc.).

It appears that the gases which are adsorbed in greatest quantity by the charcoal are approximately those most easily condensed to the liquid state; and it has been suggested that the gases are liquefied on the surface of the charcoal. In any case, the "condensed" gas is usually more chemically active than the gas in the ordinary condition.

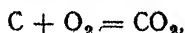
This enhanced activity is specially noticeable in charcoal (called *activated* or *active charcoal*) which has been heated in the absence of air and in presence of a little steam or oxygen. For instance, active charcoal will bring about the combination of dry hydrogen and dry chlorine at ordinary temperatures and in absence of light.

Charcoal also adsorbs solids and liquids in a similar way. A solution of litmus passes through filter paper without any noticeable change in the colour of the solution; but if the solution be filtered through charcoal, or if some recently ignited animal charcoal be boiled for a short time with litmus solution and filtered, the filtrate is colourless.

Advantage is taken of this property of animal charcoal or bone black to remove the colouring matter from many products manufactured industrially; e.g., coloured solutions of brown sugar are "bleached" on boiling with animal charcoal. The charcoal removes the brown resinous colouring matter, and the evaporated syrup furnishes white sugar; glycerine, which is brown when crude, is decolorized similarly; fusel oil can be removed from whisky by filtration through animal charcoal before the whisky is rectified. Charcoal filters are used for removing organic matter, etc., from drinking water.

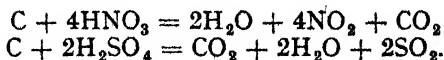
Charcoal is, chemically, the most reactive of the forms of carbon,

again probably on account of its large surface. It burns readily in excess of air or oxygen to carbon dioxide:

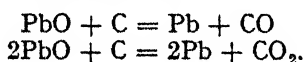


but some carbon monoxide is also formed if the supply of air or oxygen is restricted.

Charcoal reacts with many oxidizing agents as, for example, concentrated nitric acid and concentrated sulphuric acid, the reactions being represented by the equations:



These are, of course, examples of the power of charcoal to act as a reducing agent. Hence, in metallurgical industries, carbon is often used as a reducing agent (cf. manufacture of iron, page 901; zinc, page 715; tin, page 783; and lead, page 792, etc.). When a mixture of carbon with the oxide of one of these metals (litharge, for example) is heated in a crucible, either carbon monoxide or carbon dioxide is evolved and the metal remains behind:



### § 5 Coal

Coal is a complex carbonaceous material, resulting from a series of decompositions which have taken place in a restricted supply of air. High pressure also is believed to have played an important part in the process.

Geologists have potent reasons for believing that coal is of vegetable origin. The softer varieties of coal are often changed so little that their vegetable origin is easily seen. Fossil plants can be recognized, and photographs of thin slices under the microscope show clearly the vegetable character of the coal. In some of the harder varieties, the vegetable origin can only be demonstrated by analogy and comparison with varieties less modified. There is a closely graded series ranging between peat at one end, and the anthracite coals, or maybe graphite, at the other. It is convenient, however, to pick out certain members of the series as types. We thus obtain peat, lignite, bituminous, and anthracite coals. There are no hard and fast lines between these different types; the one merges into the other by insensible gradations.

The chemistry of the process of coal formation appears to be somewhat as follows:

When vegetable tissue is exposed to the air, it oxidizes and decays comparatively quickly; the gaseous products of the oxidation diffuse into the atmosphere; and the mineral constituents remain behind. If the oxidation takes place in a limited supply of air, e.g., while

submerged in a swamp or bog, the process of decomposition is rather different. Some of the carbon is oxidized to carbon dioxide, and some of the hydrogen is oxidized to water, and probably some is transformed into methane—marsh gas—etc. As a result an increasing proportion of carbon remains behind. The total weight of the organic matter decreases; and, although the total amount of mineral matter—ash—remains constant, the *percentage* amount increases.

While it is probable that the early stages of the metamorphosis are brought about by bacteria and oxidation in a limited supply of air, it is also probable that the *pressure* of the superincumbent deposits of sand, mud, etc., extending over long periods of time, are needed for the later transformations. The gases—carbon dioxide, methane, water, etc.—formed during the earliest stages of the process of conversion of vegetable tissue to coal, can escape; later, when the air is shut off, methane, etc., may be imprisoned in the coal to be released as “firedamp,” page 369, when the pressure is relieved during the mining of the coal. In some cases, the coal appears to have been *heated under pressure*. The nature of the final product, as now mined, must depend on the character of the original deposits and on the particular conditions which prevailed at the different stages of the process of transformation. The vegetable matter may have been deposited in fresh or salt water, in lakes, lagoons, seas; in marine swamps; etc. The original vegetable tissue may have been algae deposits in sargasso seas, peat bogs, vegetable accumulations on the soil in luxuriant forests, delta and drift deposits, etc. The pressure may have been comparatively small, extended over a long period of time, and applied comparatively early in the process of transformation; the pressure may have been very great and applied late in the process of conversion. An “old” coal geologically might be “young” chemically, and conversely. Geologists can sometimes form a good idea of what has happened; in other cases, they confess complete ignorance.

Coals of many different types can thus be distinguished; the following are the principal ones:

**Lignite or Brown Coal** is intermediate in type between peat and coal proper. It contains much moisture, and although it ignites easily, its calorific power is low. It usually disintegrates on exposure to the air. Extensive deposits of lignite exist on the Continent and in the U.S.A., but not in England.

**Cannel Coal**, although resembling bituminous coal in many ways, appears to have been formed differently. Some specimens yield fragments which ignite so readily that they burn like a candle (hence the name). Cannel coal is used almost exclusively for gas-making (see page 378).

**Bituminous Coal** is the commonest variety. It is black, hard and brittle and gives off large quantities of gas when heated (cf. § 15, page 377).

**Anthracite** is very hard, dense, black and brittle and exhibits little

or no trace of vegetable origin in its structure. It ignites with difficulty but its calorific power is very high.

Table XXX gives averages from a number of published analyses of different varieties of coal.

TABLE XXX.—AVERAGE COMPOSITION OF DIFFERENT TYPES OF COAL, ETC.

	Ash	Fixed carbon	Volatile matter	Moisture
Wood . . . .	1.5	25.0	53.5	20.0
Peat . . . .	1.2	29.2	51.5	18.1
Lignite . . . .	8.0	43.1	42.7	6.2
Cannel coal . .	1.5-5	30-50	50-70	3.0
Bituminous coal .	6.3	63.5	29.2	4.0
Anthracite . .	5.4	86.5	6.1	2.0

Coal was formerly regarded as a variety of carbon, but it is now known that it contains only a small proportion of uncombined carbon. This is shown to be the case since a considerable proportion of coal is soluble in pyridine (pure carbon being quite insoluble), and also since a large proportion of volatile matter is driven off on heating, comprising a large variety of carbon compounds.

### § 6 Coke

Coke is the more important solid product of the action of heat upon coal in absence of air. The whole subject of this action of heat upon coal is discussed in §§ 15-17, pages 377-386, and so the manufacturing processes, etc., need not be dealt with here.

Coke is a more or less impure form of carbon, containing from 85 to 90 per cent of that element. It is used in the manufacture of iron and steel, and in a great many metallurgical operations where its comparative freedom from sulphur and certain other impurities renders it more suitable than coal.

The properties of coke depend upon the nature of the coal from which it is obtained, and upon the way the coal is "coked." The two main varieties are *soft coke*—porous, black, brittle, ignites with difficulty, and is used for smiths' forges, etc.; *hard coke*—dark grey in colour, bright lustre, compact, metallic ring when struck, bears great pressure without crushing, used for furnace work and metallurgical operations generally.

### § 7 Graphite

Prior to 1779, molybdenum sulphide and graphite were confused together and thought to be the same substance. In that year K. W. Scheele showed that the former mineral gave a solid "acid" when burnt in air (see page 878) and evolved sulphur dioxide, whereas the behaviour of graphite in these circumstances was quite different.

There was also confusion with the native sulphides of many other elements such as antimony, manganese and lead. This is still reflected in the use of names such as plumbago and black lead for graphite.

Graphite was for a time believed to be a carbide of iron. Scheele noticed that it is deposited from molten iron in blast furnaces, and native graphite usually leaves a residue of oxide of iron when burned. This idea was not altogether given up until Brodie in 1855 prepared pure graphite, after which it was recognized as an allotropic form of carbon.

Graphite is widely distributed in different parts of the world. Large deposits occur in Ceylon and other parts of India, Eastern Siberia, United States, Canada, Bavaria, Bohemia, Moravia, Pinerola (Italy), etc., and formerly there were extensive deposits at Borrowdale in Cumberland, but the mines there are now worked out. Graphite also occurs in the form of fine crystals in many meteorites.

Graphite is manufactured artificially by subjecting amorphous carbon to a very high temperature by means of the electric furnace. The process can be understood from the diagram, Fig. 22.1.

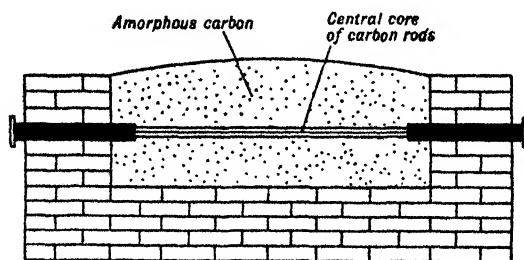
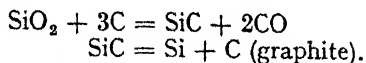


FIG. 22.1.—Graphite Furnace

A rectangular firebrick furnace is packed with a ground-up mixture of petroleum coke with coal tar or molasses, and silica or iron oxide, moulded to any desired shape. Carbon rods lead a current through the mass, which is thus heated to a very high temperature for a period of twenty-four to thirty hours. It is thought that silicon carbide (carborundum) is first formed and then decomposed, the temperature being high enough to volatilize off the silicon:



Graphite is a dark grey substance with a well-known and characteristic greasy feel; it has a lustre somewhat resembling that of a metal. It crystallizes in hexagonal plates, but as usually found it has a structure similar to that of mica, composed of a series of easily separated sheets.

•Graphite varies in specific gravity from 2 to 3. Hard graphite and soft diamonds have nearly the same specific gravity.



Chemically graphite is rather inactive, though not to the same extent as the diamond (q.v. § 8).

Graphite when heated in oxygen burns to carbon dioxide, but it undergoes no change when heated in the absence of air or oxygen. It is rather difficult to ignite.

Pure graphite is not attacked by heating it in a current of chlorine; nor by fusion with potassium or sodium hydroxide; some varieties are attacked by fused nitre. Chromic acid or a mixture of sulphuric acid and potassium dichromate oxidizes it to carbon dioxide. Neither dilute nitric nor dilute sulphuric acid attacks graphite, although some varieties swell up into worm-like structures—sometimes 12 cm. long—when the finely granulated (not powdered) graphite is moistened with nitric acid (specific gravity 1.52–1.54) in a platinum dish, and then heated. W. Luzi (1891) calls those varieties which are indifferent to the nitric acid treatment, **graphitites**; and those which swell up, **graphites**. It is generally believed that the phenomenon is a physical effect due to the absorption of acid in the capillary pores and subsequent expansion through the development of gas under the influence of heat.

The action of concentrated nitric acid on graphite is characteristic and distinguishes graphite from amorphous carbon, even though the different varieties of graphite differ considerably among themselves. Finely powdered graphite is intimately mixed with three parts of potassium chlorate and sufficient concentrated nitric acid to give a liquid mass. After heating three or four days on a water bath, the solid residue is washed with water, and dried. The treatment with nitric acid, etc., is repeated four or five times until no further change occurs. Finally, a yellow substance is obtained which retains the form of the original graphite. It is called **graphitic acid** (B. Brodie, 1859). The composition of graphitic acid is not quite clear. Diamonds are not attacked by the treatment and ordinary charcoal gives a brown mass soluble in water.

Graphite when rubbed on paper leaves a black mark—hence the term graphite—from *γράφειν* (*graphein*), to write. It is therefore used for making *lead pencils*. For this purpose the natural graphite is purified by grinding and washing so as to remove the grit. The purified graphite is mixed with a little washed clay and forced by hydraulic pressure through dies of the necessary shape. It is then stoved and cased in wood (red cedar for preference). Scaly graphite has been largely used, on account of its refractory qualities and high heat conductivity, for the manufacture of *plumbago crucibles*. The graphite is mixed with different proportions of clay and sand—e.g., 75 parts of plastic clay, 25 of sand, and 100 of graphite. The crucibles are moulded by machinery or by hand, dried, and baked at a red heat. Other refractory goods are also made from graphite. Graphite is also used as a lubricant for machinery, a coating for iron to prevent rusting, coating for goods—say plaster of Paris—to be later electrotyped,

preventive for boiler scale, stove polish, polishing powder and for gunpowder. Graphite is also used largely in making electric furnaces either alone or mixed with carborundum—thus *kryptol* is a mixture of graphite, carborundum, and clay. The resistance offered by this material to the passage of the electric current raises the temperature of the mass. If the mixture be suitably enclosed very little graphite is lost by combustion. Graphite conducts electricity very well, and electrodes of graphite are used in the electrochemical industries—e.g., in the manufacture of chlorine by electrolysis of sodium chloride, in steel-making when arc furnaces are used, and in the extraction of aluminium, magnesium and other metals. Graphite is also used for battery plates, electric-light carbons, etc. *Colloidal graphite* obtained by deflocculating graphite with an aqueous solution of tannin and also with oil, is used as a lubricant, etc., under the commercial names *Aquadag* and *Oildag*.

A recently developed and increasing use for graphite is in the construction of nuclear reactors (or atomic piles) in which it is used as a moderator, i.e., in order to slow down fast neutrons (page 172). For this purpose graphite of a high degree of purity is required as most impurities likely to be present absorb neutrons which would thus be lost to the process.

### § 8 Diamond

For long ages diamonds have been prized as ornaments on account of their beauty, rarity, and permanence. As a gem, the diamond is altogether unique, for it is separated from all other gem-stones by peculiar and distinct properties—physical and chemical.

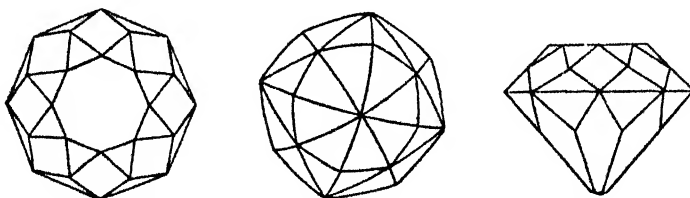


FIG. 22 2.—Diagram of Diamond—Crystal and Cut

Diamonds occur in their natural state as more or less rounded rough-looking pebbles not unlike pieces of gum arabic in appearance. The natural diamond must be cut and polished to bring out its lustre and sparkle. The diamond-cutting industry has developed chiefly in Amsterdam and Antwerp. The shape of the crystal as it leaves the diamond cutter has no relation to the natural crystalline shape. About half the diamond is lost during the cutting.

The *Cullinan* is the largest-known diamond. It was found near Pretoria (South Africa), January 1905, and weighed over  $1\frac{1}{4}$  lb.;

after cutting, it weighed about 800 carats,\* and was valued at £100,000. It was presented to the King of England by Cape Colony in 1909. The *Regent* or *Pitt diamond*, one of the French Crown Jewels, is the purest and finest known. It weighs  $136\frac{1}{2}$  carats, and was valued at F.480,000. Stones over an ounce in weight are comparatively rare.

### Occurrence

Diamonds are sparsely distributed in different parts of the world. The chief localities are South Africa, Brazil, Ural, India, Borneo and Australia. They have been found in meteorites—e.g., the Canyon Diablo meteorite (Arizona, U.S.A.) contained both black and transparent diamonds.

The chief source of diamonds at the present day is in what are known as the diamond-pipes of South Africa. These "pipes" are thought to be the shafts of extinct volcanoes, and are found to be filled with a curious type of rock called *blue-ground*. When first mined, this substance is hard, but when exposed to the weather it falls to powder and diamonds are found in the disintegrated mass.

Diamonds have proved surprisingly difficult to make artificially. In general, it is possible to obtain an element crystalline either by deposition from solution (cf. sulphur, Chapter 25) or by very slow cooling of the molten element, or by sublimation. It is only recently that carbon has been melted, and it has been found to solidify to pure graphite. It volatilizes at ordinary pressures at  $4347^{\circ}$  without melting, but the vapour condenses to amorphous carbon and not to diamond. Carbon does not dissolve in any ordinary solvent but does so to a considerable extent in molten iron. The occurrence of diamonds in supposedly volcanic shafts suggests that pressure is an essential condition for their formation. Hence, if carbon could be deposited from molten iron, under the right conditions of temperature and pressure, it seemed likely that diamonds would result. Moissan was for many years believed to have proved this. He packed a piece of iron, as pure as practicable, in a carbon crucible with sugar charcoal. The crucible was heated between the poles of an electric arc furnace. Under these conditions the iron melted and dissolved much carbon. When the temperature had reached  $3500^{\circ}$ , and the iron was volatilizing in clouds, Moissan plunged the crucible in molten lead. The sudden cooling solidified the outer layer of iron. The compression

\* Diamonds are sold by the "carat." The carat represents the Roman *siliqua* or Greek *κεράτιον*. It was  $\frac{1}{4}$ th of the golden solidus of Constantine, which was  $\frac{1}{2}$ th oz. It is now a measure of weight used for diamonds and other precious stones, and was originally  $\frac{1}{16}$ th oz. or  $3\frac{1}{2}$  grains, but it is now nearer 0.207 gram,  $\frac{1}{16}$ th oz. troy, or  $3\frac{1}{2}$  grains troy. The value of the international carat is 0.2 gram or 3.08647 grains troy. The term "carat" is derived from the carob bean, formerly used as a small weight by the diamond merchants of India. Its exact value has varied in time, and it varies in different countries. The carat is also a proportional measure of  $\frac{1}{4}$ th, and is used in stating the fineness of gold.

which the inner liquid core underwent on solidifying must have produced an enormous pressure. Hence the carbon separated from the iron under a very great pressure. After dissolving away the iron, etc., some of the carbon which remained was believed to be in the form of transparent diamonds—microscopic, it is true. More recently (e.g., Desch, 1928) some workers have concluded that Moissan could not have obtained diamonds in this way, and that the artificial production of diamonds had not at that time been achieved. The production of industrial diamonds on a commercial scale was, however, begun in the U.S.A. at the end of 1957. No details of the process have been released.

### Varieties

Diamonds are usually tinged slightly yellow. The clearest and most nearly colourless diamonds without flaw are most prized as “diamonds of the first water.” Diamonds are also occasionally coloured blue, pink, red, and green owing to the presence of traces of foreign metals. Some diamonds are dark grey and even black; they exhibit a more or less imperfect crystalline structure, and are known as *black diamonds*—boart or bort, and carbonado. *Boart* is an imperfectly crystallized black diamond which has various colours, but no clear portions, and is therefore useless as a gem; boart is used in the drilling of rocks, and in cutting and polishing other stones. *Carbonado* is the Brazilian term for a still less perfectly crystallized black diamond. It is as hard as boart, and has similar uses. Boart and carbonado are usually regarded as intermediate forms between diamonds and graphite.

### Properties

The diamond is rather brittle. It is probably the hardest substance known, although it is now believed by some that boron carbide,  $B_4C$ , is even harder. The hardness, refracting power, and other properties vary with different diamonds; and, indeed, in different parts of one diamond. The specific gravity varies from 3.514 to 3.518; carbonado, 3.50; boart, 3.47 to 3.49. Amorphous graphite has a specific gravity of 2.3; hard gas carbon, 2.356; and amorphous carbon, 1.45 to 1.70. The diamond is transparent to X-rays, whereas glass, used in imitation of the diamond, is nearly opaque to these rays. This furnishes a ready means of distinguishing imitation diamonds from the true gems.

The refractive index, about 2.4, is considerably higher than that of any other solid.

Chemically the diamond is not very active. It is insoluble in all liquids. Fused potassium hydrofluoride mixed with 5 per cent of nitre attacks the diamond slightly; a mixture of potassium dichromate and sulphuric acid oxidizes the diamond to carbon dioxide at about 200°. Unlike graphite and amorphous carbon, diamonds are scarcely attacked by a mixture of potassium chlorate and nitric acid.

Diamonds will burn in air or oxygen, but only with difficulty, the

temperature of ignition, which varies from  $700^{\circ}$  to  $900^{\circ}$ , depending upon the hardness, etc., of the particular specimen.

It is rather difficult to burn the diamond unless the temperature be maintained by, say, placing the diamond on a piece of platinum foil heated red hot by an electric current.

When burnt in air or oxygen, carbon dioxide is formed and only a trace of ash (chiefly silica and oxide of iron) is left. The combustibility of the diamond was predicted by Newton who, in 1675, arguing from the high refractory power of camphor, olive oil, amber, etc., "which are fat, sulphurous, unctuous bodies," inferred that, "a diamond is probably an unctuous substance coagulated," although he was anticipated by A. Boetius de Boot in 1609.

In 1694, Averani and Targioni of the Academy of Cimento first burnt the diamond by exposing it in the focus of a large "sun glass." Lavoisier in 1775, and H. Davy in 1814, showed that the diamond forms carbon dioxide when burnt, and unlike graphite and charcoal, it gives no aqueous vapour, showing that it is free from hydrogen and water. Hence it was inferred that *the diamond is crystallized carbon*.

### Uses

Apart from its use as a gem stone, the diamond is used industrially, particularly for making rock-drills, diamond dies for wire-drawing, diamond lathe tools, and precision grinding wheels, since it is one of the hardest substances known. It also finds application for glass-cutting, gem-engraving and so on.

## § 9 Internal Structure of the Forms of Carbon

The examination of the forms of carbon by means of X-rays, by the methods described in Chapter 13, has yielded results of great interest and importance.

It has been shown that, in the diamond, the atoms are arranged in such a way that each is at the centre of a regular tetrahedron, and is joined to four other atoms which lie at the corners of the tetrahedron. The arrangement is indicated in Fig. 22.3. The diamond thus consists of a series of interlacing hexagons (a conclusion in harmony with the theories of organic chemistry), each atom being covalently linked to four others. These facts account for the difficulty of chemical attack, for the nearness of the atoms and hence the high density, and for the great hardness of the diamond.

Examination of graphite by X-rays has shown that it consists of sheets or planes of covalently linked carbon atoms, but that the sheets are almost too far apart for them to be real chemical bonds between the atoms in different planes. The "fourth valency" is probably accounted for by resonance between single and double bonds between the atoms in the sheets. This structure accounts for the readiness with

which graphite can be cleaved along these planes as well as its softness and lubricating power. The arrangement is shown in Fig. 22.4.

Charcoal and amorphous forms of carbon in general are found to possess a graphite-like structure but the planes are much smaller and arranged in an irregular manner. This accounts for the greater reactivity, but also lends support to the view that amorphous carbon is not a distinct allotropic form.

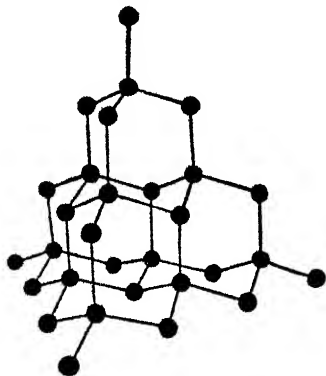


FIG. 22.3.—Structure of Diamond

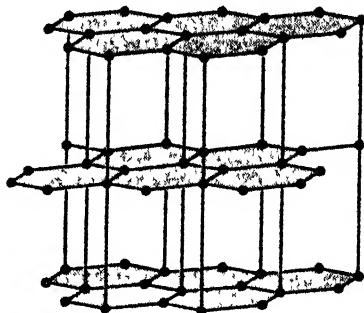


FIG. 22.4 —Structure of Graphite

### § 10 Atomic Weight of Carbon

Many determinations of the atomic weight of carbon have been made by the gravimetric synthesis of carbon dioxide by burning a known weight of diamond in a current of pure oxygen, and weighing the carbon dioxide formed by absorption in potash solution (see page 391). (For atomic weight work it is necessary to apply a correction for the expansion of the potash solution after absorption of carbon dioxide, since this alters the air displacement.)

Richards and Hoover in 1915 neutralized a known weight of very pure sodium carbonate with hydrobromic acid, thus forming sodium bromide, which was precipitated and estimated in the usual manner of the Harvard determinations (see Chapter 7, pages 105–108). In this way they obtained the value 12.003.

Physical determinations, by the method of limiting density, have been made using carbon monoxide and methane. Gray and Woodhead in 1933 obtained a value very close to 12.01 from the limiting density of carbon monoxide. Similar experiments by Cawood and Patterson (1936) with carbon dioxide, ethylene and carbon tetrafluoride led to the value of 12.011.

This value has been confirmed from observations of the relative abundance of the two isotopes,  $^{12}\text{C}$  and  $^{13}\text{C}$ , and is the one recommended by the International Committee at present (1959).

The *equivalent weight* of carbon is approximately 3; but it is known that the atomic weight is four times this value, viz., 12 approximately, since this is the smallest weight of carbon found in one molecular weight of any of the very numerous volatile organic compounds whose vapour density (and hence molecular weight) have been determined.

### § 11 Hydrocarbons. Methane

Several hundred compounds of carbon and hydrogen are known, and their study belongs to Organic Chemistry. They can be arranged in a few series, the members of which have many properties in common, and it is convenient to consider the first members of three of these series in Inorganic Chemistry. These three hydrocarbons are:

Methane	$\text{CH}_4$
Ethylene	$\text{C}_2\text{H}_4$
Acetylene	$\text{C}_2\text{H}_2$

#### Methane, $\text{CH}_4$

##### Occurrence

This gas, methane, occurs naturally as *natural gas* and *firedamp*; and it is also evolved from decomposing vegetation in ponds and marshes. Hence it is sometimes known as **marsh gas**.

Natural gas is found associated with oil, or petroleum, which is a complex mixture of hydrocarbons, the simpler constituents being gaseous at ordinary pressures. These gaseous constituents are known as natural gas, and contain a large proportion of methane.

The chemical processes believed to take place in the formation of coal have been discussed on page 359, where it was mentioned that methane is formed and often imprisoned in the coal, sometimes under considerable pressure. When the coal is mined, this gas naturally escapes and, since it forms an explosive mixture with air, it is a source of danger and has given rise to many serious explosions. Among miners the gas is known as *firedamp*.

Methane appears to be a product of the gradual decay of vegetable matter in a very limited supply of air, and escapes in bubbles when the marshy bottoms of stagnant pools are disturbed. The gas can be collected and identified as methane. Sewage sludge on fermentation evolves a similar gas which is used in some places as a source of fuel.

Methane is also an important constituent of coal gas, comprising from 25 to 40 per cent of the gas which results from the destructive distillation of coal.

##### Preparation of Methane

Carbon and hydrogen unite slowly at a dull red heat with the formation of methane, but the amount of methane formed is too small for this to be a practicable method of preparation.

Methane is usually prepared in the laboratory by the following process. A quantity of fused (anhydrous) sodium acetate is intimately mixed with about three times its weight of soda lime (an intimate mixture of sodium hydroxide and slaked lime obtained by slaking quicklime with sodium hydroxide solution instead of with water) in a mortar; and the mixture transferred to a copper tube, *A* (Fig. 22.5). The

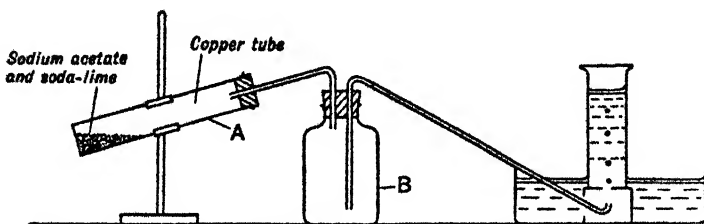
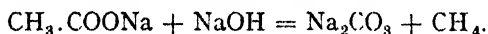


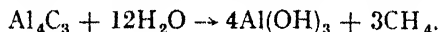
FIG. 22.5.—Preparation of Methane

tube is connected to an empty bottle *B*, arranged as shown, so as to prevent water being sucked back into *A* during the course of the experiment. The gas formed when *A* is strongly heated is collected over water as shown. The reaction may be represented by the equation .

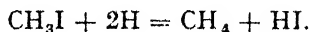


Sodium hydroxide itself is not used on account of its fusibility.

The gas prepared by this process is not very pure and contains about 90 per cent of methane, but the mode of preparation is useful for ordinary purposes. For instance, this gas burns with a luminous flame, whereas pure methane burns with a non-luminous flame. A fairly pure gas—mixed with a little ammonia and acetylene—is formed by the action of water on commercial aluminium carbide:



The gas can be washed free from acetylene by means of an ammoniacal solution of cuprous chloride. When pure methane is required, methyl iodide,  $\text{CH}_3\text{I}$ , is reduced by nascent hydrogen formed by the action of a mercury : aluminium couple, or a copper : zinc couple on water or alcohol, thus:



This method of preparation is discussed in works on organic chemistry.

Methane is now being manufactured from water gas (see page 400).

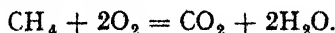
### Properties

Pure methane is free from colour, and is without smell. The gas prepared by the ordinary process usually has a slight smell owing to the presence of impurities. Methane is lighter than air. 100 volumes of water at  $0^\circ$  dissolve  $5\frac{1}{2}$  volumes of the gas; and at  $20^\circ$ ,  $3\frac{1}{2}$  volumes.



Methane is rather more soluble in alcohol. It liquefies at  $0^{\circ}$  under a pressure of 140 atmospheres. The liquid boils at  $-161.5^{\circ}$ , and solidifies at  $-182.5^{\circ}$ . Methane has no well-defined physiological action on the system other than diluting the oxygen and so inducing suffocation.

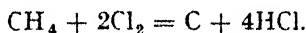
Pure methane burns with a pale blue, almost non-luminous flame, forming carbon dioxide and water:



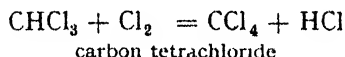
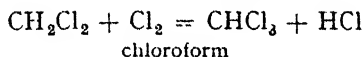
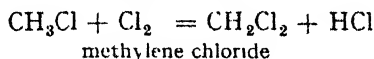
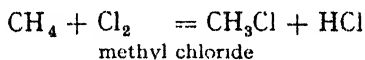
It is a non-supporter of combustion, as is shown by plunging a lighted taper into a jar of the gas (held mouth downwards). The taper is extinguished, while the gas burns at the mouth of the jar.

Methane forms explosive mixtures with air, even when present only to the extent of 5 or 6 per cent.

Apart from its combustibility methane is chemically very stable and attacked by but few reagents. It is attacked by chlorine, the nature of the products depending upon the conditions. A mixture of methane with excess of chlorine explodes when exposed to direct sunlight, carbon being deposited:



When a mixture of equal volumes of chlorine and methane is exposed to *diffused daylight*, they gradually react forming methyl chloride,  $\text{CH}_3\text{Cl}$ . If more chlorine be present it gradually replaces all the hydrogen:



This process of replacing one or more atoms in a molecule by equivalent atoms is called **substitution**. The formation of these should be contrasted with the **addition** compounds of ethylene (see page 374). Methane is unattacked by other chemical reagents except under extreme conditions.

### § 12 Formula of Methane

The formula of methane, and of other gaseous hydrocarbons, can be found from the results of exploding a measured volume of the gas with excess of oxygen in an eudiometer. The water formed condenses and causes a contraction which determines the amount of hydrogen present since it is equal to the volume of the steam formed. The carbon dioxide also formed can then be absorbed by potassium

hydroxide solution and the resulting contraction measured. The calculation of the formula from the data so obtained is illustrated by the following example:

*In an experiment 10 c.c. of methane were exploded with 40 c.c. of oxygen. After cooling the volume of the mixture was 30 c.c. After absorbing the carbon dioxide by means of caustic potash solution the volume of unused oxygen remaining was 20 c.c. What is the formula of methane? (All volumes have been reduced to S.T.P.)*

The results of the experiment show that one volume of methane reacts with two volumes of oxygen, and that one volume of carbon dioxide is formed.

Hence, if the formula of methane be  $C_xH_y$  we have (Chapter 8, page 118):

$$x = 1 \text{ and } x + \frac{y}{4} = 2$$

$$\therefore y = 4$$

so that the formula of methane is  $CH_4$ .

### § 13 Ethylene, $C_2H_4$

#### Occurrence and Preparation

Ethylene was discovered by J. J. Becher about 1669, and its properties were distinguished from ordinary inflammable air by the Dutch chemists J. P. Deimann, A. P. van Troostwijk, N. Bondt, and A. Lauwerenburgh (1795). These chemists also showed that the gas contained carbon and hydrogen. It was clearly distinguished from methane in 1805 by W. Henry.

Ethylene occurs in natural gas (page 369). Some analyses of "pit gases" show that up to 6 per cent of this gas may occur in the air in coal pits. This gas is also obtained when coal or wood is heated in closed vessels, and coal gas contains from 4 to 10 per cent of ethylene.

Ethylene is usually prepared by the action of concentrated sulphuric acid on alcohol. This is an interesting reaction since, according to the conditions, either ethylene or ether may be formed. This latter substance is studied in organic chemistry.

For the preparation of ethylene 30 ml. of alcohol are mixed with 80 ml. of concentrated sulphuric acid in a large flask, through the neck of which passes a tap-funnel and a thermometer (with its bulb in the liquid) as well as a delivery tube. The mixture is heated to  $160^\circ$  on a sand bath, when ethylene is formed along with sulphur dioxide, carbon dioxide, a little ether, etc. The gas is washed by passing it through a bottle containing strong sodium hydroxide solution and collected over water (see Fig. 22.6). The supply of gas can be maintained by adding slowly a mixture of equal volumes of alcohol and concentrated sulphuric acid through the tap-funnel.

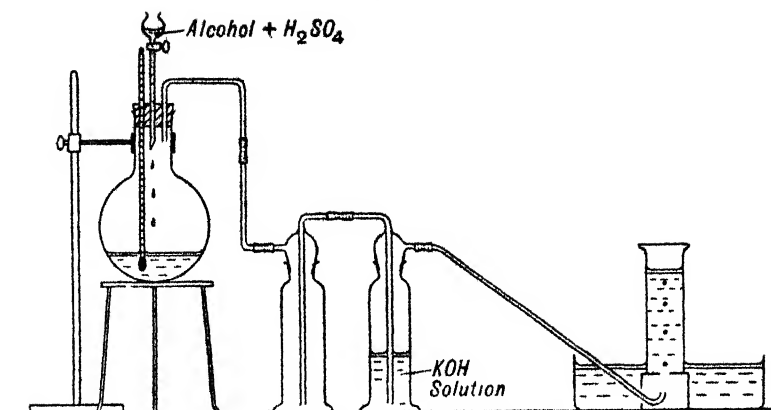
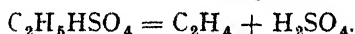
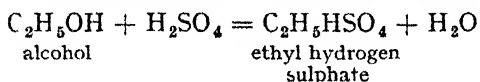


FIG 22 6 —Preparation of Ethylene

The reactions which take place may be represented by the equations:



The former reaction takes place at ordinary temperatures, but the ethyl hydrogen sulphate formed breaks up into ethylene and sulphuric acid at temperatures above  $150^\circ$ . Summarizing the two equations, we have



and so the process is sometimes thought of as a dehydration of alcohol.

Syrupy phosphoric acid can be used in this experiment instead of sulphuric acid, but a temperature of  $200^\circ$ - $220^\circ$  is then required.

Ethylene is now produced in large quantities in the "cracking" of petroleum. It is used in the U.S.A. as a fuel and as a source of alcohol. It is also employed for the artificial ripening of citrus fruits and as an anaesthetic.

### Properties

Ethylene is a colourless gas with a peculiar ethereal odour. It has nearly the same density as air. 100 volumes of water at  $0^\circ$  dissolve 25.7 volumes of the gas, and at  $20^\circ$ , 15 volumes; the gas is nearly 13 times as soluble in alcohol. Ethylene liquefies at  $0^\circ$  under a pressure of 43 atmospheres; the liquid boils at  $-103.7^\circ$ , and solidifies at  $-169.2^\circ$ . The gas behaves like methane towards a lighted taper, but it burns with a luminous smoky flame unless it be diluted with hydrogen or methane. Ethylene is decomposed at a high temperature. This is

illustrated by passing the gas through a bulb-tube of hard glass. When all the air has been expelled, if the bulb be heated in the blowpipe flame, a mirror-like deposit of carbon can be formed in the interior of the bulb.

Ethylene forms an explosive mixture with air and the explosion is even more violent than with methane.

If a mixture of hydrogen and ethylene be passed over reduced copper, between  $180^{\circ}$  and  $300^{\circ}$ , the ethylene,  $C_2H_4$ , is reduced to **ethane**,  $C_2H_6$ , a gas resembling methane in many of its properties. Finely divided nickel can also be used as a catalyst.

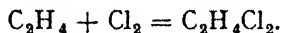
The formula for the gas can be determined in the same way as that of methane (q.v.). In this way it is found to be  $C_2H_4$ , which is confirmed by vapour density measurements which show that the molecular weight is 28. (Cf. also page 118.)

The graphic (or structural) formula of ethylene is usually written with a "**double bond**":



Most of the evidence for this type of linkage belongs to the realm of organic chemistry. It appears to involve a state of strain in the molecule, and hence a compound possessing a linkage of this kind is reactive and forms **addition products**.

Thus, one molecule of ethylene readily combines with a molecule of chlorine when equal volumes of the two gases are mixed, forming an oily liquid known as ethylene dichloride, the formula of which is  $C_2H_4Cl_2$ :

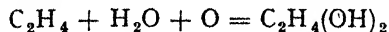


One of the earliest properties of ethylene to be observed was the formation of this oil which gave rise to the name *olefiant* (= oil forming) *gas* for ethylene.

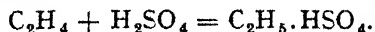
Ethylene will react similarly with hydrobromic and hydriodic acids:



It is also readily oxidized by oxidizing agents, such as potassium permanganate:



and is absorbed by very concentrated or fuming sulphuric acid forming ethyl hydrogen sulphate:



Ethylene is thus a very reactive substance and forms, as a rule, **addition products**. In this respect its behaviour is in marked contrast with that of methane which is chemically inert and, when it reacts at all, forms substitution products.

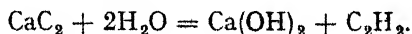
### § 14 Acetylene, $C_2H_2$

This gas was discovered by E. Davy in 1836. He obtained it by the action of water on the black mass formed as a by-product in the manufacture of potassium.

#### Preparation

Acetylene is formed in small quantities by sparking carbon electrodes in an atmosphere of hydrogen. It is also found in small quantities in the gases issuing from a bunsen burner which has "struck back."

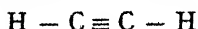
The most convenient and usual method for preparing acetylene is by the action of water on calcium carbide (page 696). The reaction may be represented by the equation:



In the laboratory the reaction can be conveniently carried out in an apparatus such as is indicated in Fig. 22.7.

When prepared in this way the gas contains small traces of sulphur and phosphorus compounds, ammonia, etc., but it is usually pure enough for experimental work. The gas can be purified from the most objectionable impurities by passing the gas through a wash-bottle containing a solution of copper sulphate acidified with sulphuric acid. This removes ammonia and compounds of phosphorus or sulphur.

The formula for acetylene, determined in the same way as that of methane, is  $C_2H_2$ , and the graphic formula is written



since it exhibits the unsaturated behaviour of ethylene in a double degree.

#### Properties

Acetylene is a colourless gas which, when pure, has an ethereal odour which is not unpleasant. As usually prepared and purified the gas contains traces of impurities which impart to it an offensive smell reminding one of garlic. Acetylene is rather lighter than air. 100 volumes of water at  $0^\circ$  dissolve 173 volumes of acetylene; and at  $20^\circ$ .

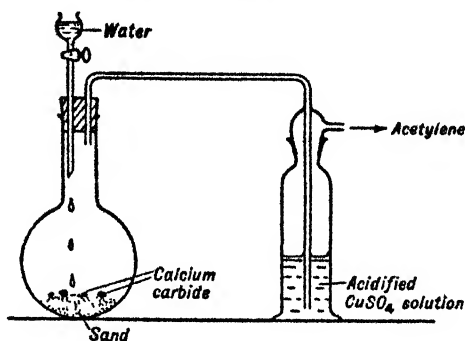


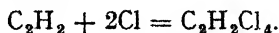
FIG. 22.7 — Preparation of Acetylene

103 volumes of the gas. Alcohol dissolves about six times its own volume at ordinary temperatures; and the gas is absorbed by fuming sulphuric acid. Acetylene can be hydrogenated (reduced) to ethylene,  $C_2H_4$ , and to ethane,  $C_2H_6$ , if it be mixed with hydrogen, and passed over finely divided nickel. Acetylene is poisonous and soon induces headache. On cooling, acetylene forms a white solid which sublimates at  $-84^\circ$  at ordinary pressures.

Acetylene burns with a luminous smoky flame, but, like the other hydrocarbon gases, it extinguishes a lighted taper plunged into the gas. If acetylene be burned from a jet with a very fine aperture the flame is not smoky, but it is exceedingly luminous. In most acetylene burners the gas issues as two small jets so arranged that they strike against one another and produce a flat flame. Other holes are located so that air is drawn in and mixed with the gas as it rushes through the nozzle. The great luminosity of the acetylene flame, coupled with the easy preparation of the gas from "carbide," led to the extensive use of acetylene for lighting at one time, but with the development of electric lighting this use has declined.

Acetylene is violently explosive when mixed with  $2\frac{1}{2}$  times its volume of oxygen. The gas cannot be safely stored under a greater pressure than 2 atmospheres—30 lb. per square inch—because it is then liable to explode violently by mere shock. The method of storing acetylene under pressure is to employ a solution of the gas in acetone, which, under a pressure of 12 atmospheres, dissolves 300 times its volume at ordinary temperatures. It is stored and transported in steel cylinders, containing kapok and partially filled with acetone, when required for industrial operations such as welding, cutting steel, etc., as mentioned below.

Acetylene resembles ethylene in the readiness with which it forms additive compounds with chlorine, oxidizing agents, etc. When mixed with chlorine, it explodes violently; but under regulated conditions acetylene tetrachloride results.



Acetylene tetrachloride is now manufactured by passing chlorine and acetylene alternately into sulphur chloride containing a little reduced iron, and is sold under the name *Westron*.

Acetylene reacts with solutions of some metallic salts with the formation of explosive compounds known as acetylides. The most familiar of these is cuprous acetylide, which is formed as a red precipitate when a current of acetylene is passed through an ammoniacal solution of cuprous chloride. This precipitate has the formula  $Cu_2C_2 \cdot H_2O$  and, when dried, forms the acetylide  $Cu_2C_2$ . Similar acetylides are formed by silver and mercury. The action of dilute acids on these compounds produces pure acetylene.

## Uses

The use of acetylene as an illuminant has already been mentioned.

*Oxy-acetylene blowpipes* are used for welding pieces of iron and steel together under conditions where forge welding is impracticable. The flame is produced by burning a mixture of the two gases delivered into special blowpipes under pressure (the acetylene from an acetone solution of acetylene under pressure). The flame at the apex of the small central white cone has a temperature of about  $3000^{\circ}$ . At that point, the flame is almost entirely carbon monoxide surrounded by a jacket of hydrogen. The temperature at the apex of the flame is too high to allow the hydrogen to combine with the oxygen. The flame is therefore hot enough to melt iron and steel, and yet sufficiently reducing to protect the fused metal from oxidation while the welding is in progress.

It is also used, particularly at Niagara Falls and at Visp in Switzerland, as the starting point for the manufacture of acetic acid and a large range of other organic chemicals.

## § 15 Coal Gas

Coal gas consists of a mixture, in varying proportions, of hydrogen, carbon monoxide, methane and other hydrocarbons, and is the gas which results from the distillation of coal out of contact with the air. The formation of such a gas is referred to by writers as early as the seventeenth century, but its use as an illuminant was not developed until the end of the eighteenth century. Its use was introduced by William Murdoch in 1792 and in 1798 he installed a plant for the lighting of Boulton and Watt's engineering works at Soho, Birmingham, by gas.

When coal is heated in closed vessels to about  $400^{\circ}$ , it is carbonized, and a comparatively small quantity of gaseous, and a relatively large quantity of liquid, products are obtained. If the temperature of distillation be raised, the quantity of liquid products decreases, and the quantity of gaseous products increases. In other words, more gas and less tar is obtained. The gas obtained by the high-temperature distillation has less illuminating power, when burned at a jet such as the flat-flame or fish-tail burner. In modern practice, there is a tendency to raise the temperature of distillation, thus sacrificing illuminating power for quantity (cubic feet of gas per ton of coal). Since nowadays it is the heating value of the gas which is important (for even when used for lighting it is in conjunction with incandescent mantles), the lower illuminating power of the gas is not a disadvantage.

Experiments are now being conducted, however, with low-temperature distillation (i.e., at a temperature of  $300^{\circ}$ – $400^{\circ}$  C.) because of the improved yield of volatile liquid products (benzene, etc.) which are then produced and which are valuable for use as motor spirit, etc. In ordinary gasworks practice, however, a temperature of about  $1000^{\circ}$  C. is employed.

When coal is heated in this way there is formed:

- (i) A mixture of gases, consisting mainly of hydrogen, methane, carbon monoxide and a little ethylene.
- (ii) A liquid portion. This separates into two layers, viz.:
  - (a) an aqueous layer containing ammonia, ammonium sulphide, phenol (carbolic acid), pyridine and small quantities of other organic compounds;
  - (b) a layer of "tar" insoluble in water consisting of a large number of hydrocarbons (e.g., benzene, toluene, naphthalene) and related organic compounds of great technical importance.
- (iii) A non-volatile residue of coke.
- (iv) A hard greyish-blue form of carbon known as **gas-carbon** adhering to the walls of the retort.

The approximate amounts of the various products obtained from one ton of coal are:

Coal gas	.	.	10,000–12,000 cu. ft.
Tar	.	.	115 lb.
Ammonia	.	.	7 lb.
Coke	.	.	1550 lb.

### § 16 Coal Gas Manufacture

The details of the plant in use at various gasworks differ considerably, in particular in the arrangement of the retorts, but the chemistry of the process is essentially the same in all. Different types of retort are illustrated by Plate 16 and Fig. 22.8, and the general layout by Fig. 22.9.

#### 1. The Retorts

The coal is distilled in fireclay or silica retorts, which may be set horizontally or in an inclined position, or vertically. When horizontal or inclined the retorts are  $\Delta$ -shaped in section and uniform throughout their length; when vertical they are rectangular and usually taper somewhat towards the top.

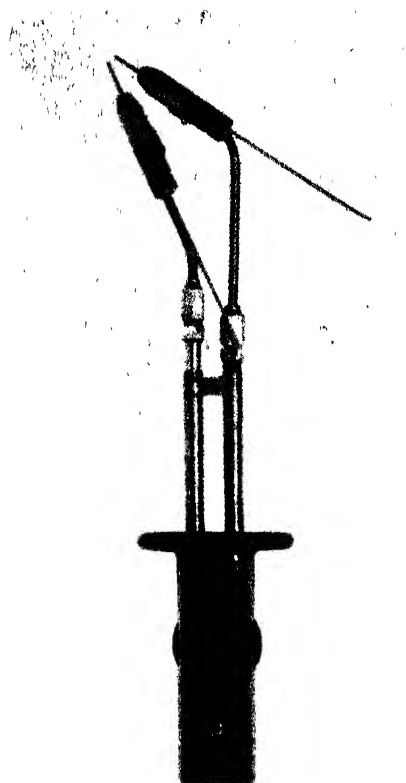
When horizontal retorts are used they are fixed to an iron furnace front, each fitted with a door and connected with a vertical exit pipe—the *ascension pipe*—for the escape of volatile products. The retorts are arranged in banks of five or more, heated by a single furnace.

Each group of retorts is heated by **producer gas** formed by passing air through a bed of hot coke in a special furnace underneath. (See page 399 for a fuller account of producer gas, which is essentially a mixture of carbon monoxide and nitrogen.)

The volatile products pass from the retort into the *hydraulic main* which contains condensed coal tar and water. This main runs horizontally over the front of the bench of retorts, and all the retorts discharge into it. The gas is here partly cooled, and some tar and water are

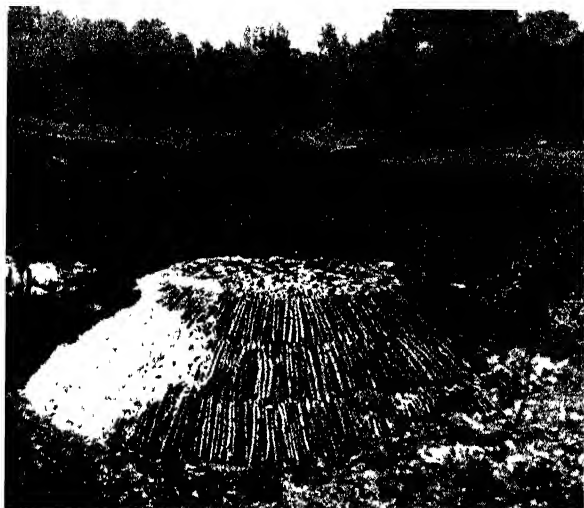


13. Atomic hydrogen blowpipe  
(see pp. 296, 298)

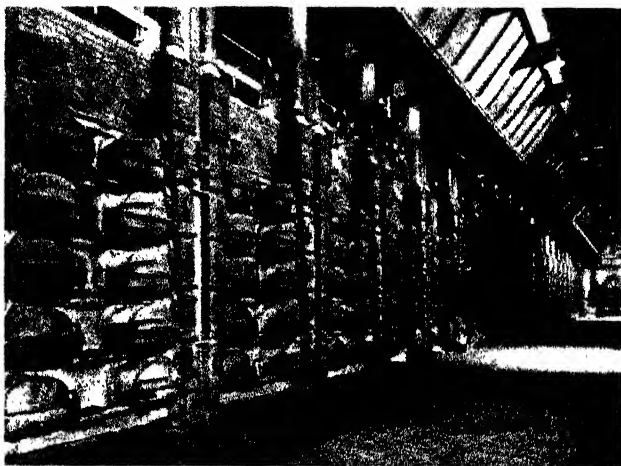


14 Stalactites and stalagmites in the  
Jenolan caves, N.S.W.

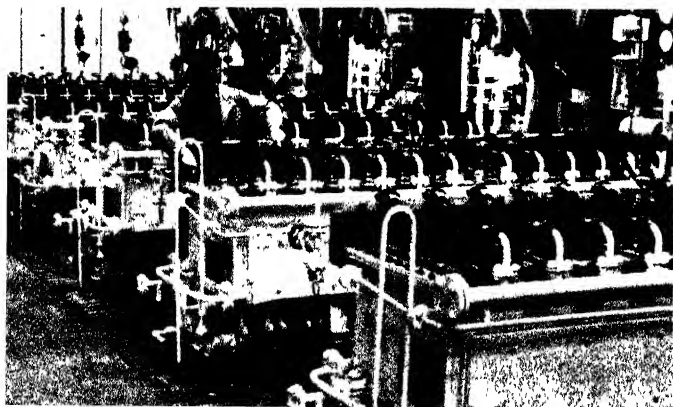




15 Meiler in course  
of construction



16 Retorts for gas making



17. Modern fluorine  
cellroom

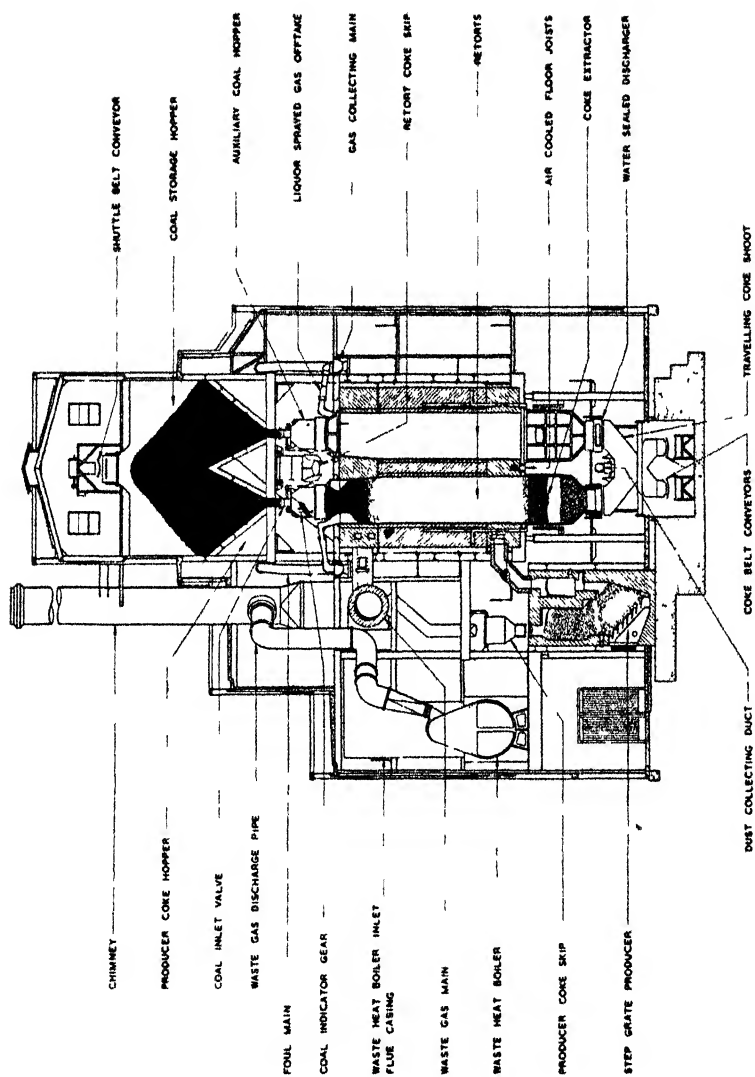


FIG. 22 8.—Cross-section through a Modern Continuous Vertical Retort Installation.  
(By courtesy of the Woodall-Duckham Construction Company Ltd.)

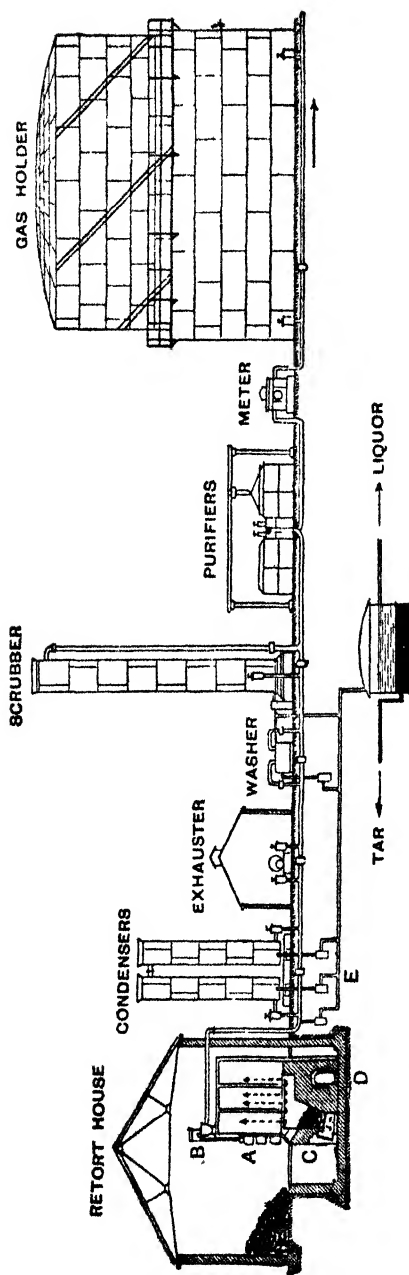


FIG. 22 9.—General Diagram of Gasworks  
 From Lowry and Cavell's Intermediate Chemistry, by permission of Messrs Macmillan & Co Ltd.

condensed from the hot gas. The pipe leading the gas from the retort dips into the liquid in the hydraulic main, and so prevents the gas from passing back when the retorts are recharged. The liquid in the hydraulic main is kept at a constant level by leading the excess into the *tar well*. With horizontal retorts containing about 8 cwt. of coal, the distillation will be complete in about 8 hours. The newest silica retorts hold up to 1 ton and carbonization may then take up to 12 hours. The coke is pushed or raked from the retort, and quenched with water to prevent further combustion. Another charge of coal is quickly introduced into the retort.

The arrangement of horizontal retort settings is illustrated by Plate 16.

When vertical retorts are employed they are arranged in a manner which may be understood from Fig. 22.9. They are now usually made of silica brick. In these the coal enters at the top from a special hopper in a slow continuous stream, while the coke is similarly removed from the bottom. A non-caking coal must be used in these retorts to prevent sticking. The advantages of vertical retorts are continuous operation, and the by-products include a more fluid tar and a larger proportion of ammonia. Steam is usually introduced into the base of the retorts; this steaming produces a proportion of water gas at the same time as the coal is distilled and also cools the coke ready for discharge at the bottom of the retort. (Cf. also page 400.) Vertical retorts are heated by producer gas in a similar manner to the horizontal type.

## 2. The Condensers

The hot impure gases pass from the hydraulic main into condensers. Here the gas passes up through vertical tubes which are surrounded by a stream of cold water. The gas is thus cooled still further, and more tar is condensed and run to the tar well. The condensed liquid in the tar well separates into two layers—the lower layer is *gas tar*; and the upper aqueous solution containing ammonia and ammonium salts is the *gas liquor*. The gas is drawn from the hydraulic main through the condensers by means of an *exhaust pump* which reduces the pressure in the retort; it also regulates the pressure of the gas sent along to the rest of the plant.

## 3. The Scrubbers

In modern works all the tar is removed from the gas in the condensing plant, but the gas still contains sulphur compounds, carbon dioxide and some ammonia. In one form of scrubber, a tower is filled with trays charged with coke or pebbles. The tower has a partition so that the gas flows down one side of the tower and up the other. A spray of water trickles down the coke. The gas in passing through the coke is broken up into small bubbles and washed free from ammonium compounds by the water. Rotary scrubbers are now used also and are more efficient and occupy less room than the older types.

The liquid from the scrubbers is drawn off from time to time and mixed with the gas liquor from the tar well.

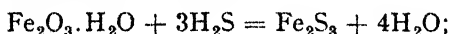
In some plants, particularly coke-ovens (see page 386), *direct ammonia recovery* is used. The gas is air-cooled to about 80° only, residual tar fog removed by electrostatic precipitators, and the remaining gas, still above its dew-point, passed through sulphuric acid in lead-lined containers. Ammonium sulphate is formed and removed continuously as a solid.

#### 4. The Purifiers

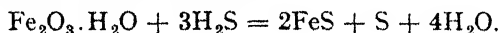
Some of the hydrogen sulphide, hydrogen cyanide and carbon dioxide in the gas combine with the ammonia and are removed in the scrubbers. The gas still contains hydrogen cyanide, hydrogen sulphide and carbon disulphide. The remainder of the hydrogen cyanide is usually removed by washing the gas with an alkaline liquor containing ferrous sulphide or hydroxide in suspension:



The gas is then freed from hydrogen sulphide in the *purifiers* which consist of a series of low rectangular iron tanks fitted with horizontal shelves or grids. (Recently experiments have been undertaken with tower-purifiers using specially active forms of iron oxide enabling a high rate of gas-flow to be maintained.) The shelves are loosely packed with a layer of ferric hydroxide ("bog iron ore")— $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The ferric hydroxide forms ferric sulphide:

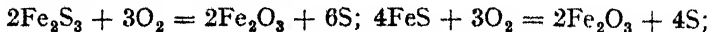


or ferrous sulphide and free sulphur:



If the gas has not been washed to remove hydrocyanic acid, this will react with the ferric oxide of the purifiers, forming ferric cyanide and, ultimately, prussian blue.

When the mixture is fouled it is placed in a heap for about twenty-four hours and then spread out in layers twelve inches deep. The layers are turned over repeatedly to expose fresh surfaces to the action of the air. The black iron sulphides are oxidized by exposure to the air, and free sulphur separates:

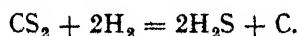


the net result is that the hydrogen sulphide of the gas is converted into free sulphur, and the ferric oxide is revived ready to be used again. This alternate fouling and oxidizing of the "iron" is repeated about sixteen times when so much sulphur accumulates—55 per cent—that it is no longer economical to use the oxide again. This *spent oxide* is sold to the manufacturer of sulphuric acid, and used as a source of

sulphur. Recently it has also been used as a source of iron, being worked up after a preliminary treatment for blast-furnace use.

The possibility of using liquid purifiers, in which the gas is washed with a solution of sodium carbonate or ammonia, is now being advocated but this method has, so far, to be operated in conjunction with ferric oxide for the final purification.

The gas still contains a little carbon disulphide which is difficult to remove and whose presence is deleterious owing to the production of sulphur dioxide when it is burned. One process for its removal consists of passing the gas, before it goes to the purifiers, over a nickel catalyst at  $450^{\circ}$ . The carbon disulphide reacts with some of the hydrogen present, forming hydrogen sulphide which is removed in the purifiers:



The use of active carbon and intensive oil washing for the removal of the last traces of sulphur compounds have also been tried with success.

The gas emerging from the purifiers is then freed from benzene, and any naphthalene not condensed earlier, by washing with oil or by passage over activated charcoal. In modern works the gas is then dried by passing through concentrated calcium chloride solution. This prevents condensation of water in the mains.

## 5. The Gasholder

The purified gas next passes through a large meter which records its volume and then into the familiar gasholder. This is usually an enormous cylindrical iron tank which floats in a cistern of water, covered with a layer of oil if the gas has been dried, and rises, or falls, as gas enters, or leaves. The use of waterless gasholders in which the gas is confined in an iron tower under a large "piston" sealed by flowing tar has been developed of late years. From the gasholder the gas passes to the *governor*, where its pressure is regulated, and then to the supply mains for use.

The gas so obtained has approximately the following composition:

Hydrogen . . . .	45 per cent
Methane . . . .	35 " "
Ethylene . . . .	4 " "
Carbon monoxide . . . .	8 " "
Carbon dioxide . . . .	2 " "
Nitrogen . . . .	$5\frac{1}{2}$ " "
Oxygen . . . .	$\frac{1}{2}$ " "

Before being supplied to the public a proportion of water gas, sometimes enriched or carburetted (pages 370-1), is very generally added. This has the effect of increasing the percentage of carbon monoxide and decreasing that of methane, etc. The gas supplied to the public thus has, as a rule, only a basis of coal gas proper and contains a much higher percentage of carbon monoxide (usually between 15 and

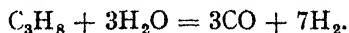
20). It is therefore often called "town gas" since the name "coal gas" is held to mean the purified, but otherwise unaltered, product of the distillation of coal. On account of the very poisonous nature of carbon monoxide, modern town gas is more dangerous if allowed to escape than true coal gas, and so the very greatest care is necessary to prevent leakage in confined spaces.

The gas industry is in a period of rapid change and development. The supply of suitable gas-coal for use with the traditional methods is running short and so methods for using other types of coal and other sources of gas are being developed. One such method is the **Lurgi** process and a large plant operating this method is now being erected at Westfield, near Loch Leven in Scotland. This method allows for complete gasification of the coal and can utilize coals not suitable for normal methods of carbonization. It consists of passing steam at a pressure of 20–30 atmospheres through a bed of coal, maintained at a sufficiently high temperature by addition of oxygen to the steam. By suitable control a gas consisting of hydrogen, carbon monoxide and methane results which can be used (after further enrichment, if necessary) in place of ordinary town gas. At Westfield it is proposed to use butane, from the nearby oil refinery at Grangemouth, for this enrichment.

The tail gases of petroleum refineries are also finding increasing application in the gas industry and very recently the practicability of transporting methane, in the liquid state, in specially designed ships, has made possible another source of raw material since methane is available in quantity, almost as a waste product, in North America.

Methane and the tail gases mentioned (which consist of a variety of hydrocarbons) have a higher calorific value than that of normal town gas and their characteristics are such that they cannot be burned efficiently in apparatus designed and adjusted for the latter. Before being supplied to the public they are, therefore, subjected to a process known as *reforming* by which a larger volume of gas, of lower calorific value, is produced which is suitable for use *pari passu* with ordinary town gas.

Reforming is effected either by simple cracking at high temperature or, more usually, the hydrocarbon gases are made to react with steam or oxygen or both. Complete reforming would involve the conversion of the hydrocarbons entirely into carbon monoxide and hydrogen; e.g., for propane,



The operation is sometimes carried out in a carburetted water gas plant, suitably modified, such as is in common use in many gasworks (see page 401). Some types of reforming plant work on the principle of partial combustion with the use of a catalyst. A controlled mixture of hydrocarbons, steam and air is passed through the catalyst bed producing a mixture of carbon monoxide and hydrogen (with some nitrogen from the air). Nickel is a common catalyst for this purpose usually supported on a refractory base such as alumina or kieselguhr.



The use of liquid butane, transported in steel cylinders and reformed in a water gas plant, is being proposed for the supply from small gas-works in areas where linkage to the high-pressure long-distance mains, now being laid, is not practicable.

### § 17 By-products of Gas Manufacture

As stated above (page 378), coal gas is only one of the numerous products of the operations described in the preceding section. Along with it are produced numerous by-products. Among these may be mentioned gas carbon, tar, ammonia, cyanides and coke.

**Gas Carbon** is a hard dense deposit of almost pure carbon which gradually collects on the inside of the retort. It is a good conductor of electricity, and is used for the manufacture of arc lamp carbons, and for batteries. **Tar**—gas tar, coal tar—is a black, viscid, foul-smelling liquid used as a protective paint for preserving timber; making tarred paper, waterproofing masonry, etc. Tar is a mixture of many organic substances which are separated by distillation at different temperatures. It furnishes carbolic and creosotic oils, benzene, naphthalene, anthracene, etc. Benzene is a most interesting compound discovered by M. Faraday and it has given rise to new and important branches of industry. It is used in the manufacture of aniline dyestuffs, flavouring essences, perfumes, oils, etc. The residue after distillation is "pitch." Artificial asphalt\* is a solution of pitch in heavy tar oils, and is used in making hard pavements, varnish, etc. **Ammonia**—the ammoniacal liquid is boiled with milk of lime and the expelled ammonia is mixed with sulphuric acid. The tarry matters are separated, and the solution of ammonium sulphate is evaporated and crystallized for the market.

This subject is further referred to in Chapter 23. **Cyanides**, which are of value, are obtained as described above. The utilization of the cyanides recovered is discussed on page 633.

**Coke**, as explained in § 6 of this chapter, is a valuable fuel and is in great demand for metallurgical and other industrial operations (see also producer gas, page 399, and water gas, page 400). As a consequence, large quantities of coal are carbonized for the direct production of coke in order to supplement the gasworks supply. This is carried out in plant known as coke ovens.

Coke ovens are of two main types: the older being known as **Beehive ovens** on account of their shape, and the more modern as **Recovery ovens**.

The **Beehive oven** consists of a covered mound of brickwork in which the coal is partly burned in a limited supply of air (cf. charcoal burning, page 356). It produces an excellent coke, but all the volatile products are lost and it is wasteful.

\* This must be distinguished from the natural asphalt obtained from the famous pitch lake in Trinidad.

**Recovery ovens**, such as the Simon-Carves and Becker ovens, make use of fireclay retorts not unlike those used in coal-gas manufacture. Fig. 22.10 is a diagram of a section of such an oven. The coal is heated in these retorts and gives off a mixture of products as in gas manufacture. Part of the gas evolved is used for heating the retorts, being mixed for this purpose with preheated air. This air derives its heat from the hot gases from the furnace by way of a heat-exchanger. The gas evolved from the retorts is cooled to separate the tar, and scrubbed to remove ammonia, etc., before being burned. Because of the value of the numerous by-products, recovery ovens are displacing the beehive type. Recently there has been established in the neighbourhood of Sheffield, where there are numerous coke ovens in operation, a gas-grid linking up the various plants and making a very cheap supply of gas available for use in the nearby towns.

### § 18 Oil from Coal

Of recent years processes for the production of oil from coal have become increasingly important. Two methods have been developed, viz., the direct hydrogenation of suitable coal, and the Fischer-Tropsch process which utilizes water gas.

The former process used by Imperial Chemical Industries consists in treating a paste of powdered coal and heavy oil from a previous operation with hydrogen at  $450^{\circ}$  and a pressure of 250 atmospheres in presence of a catalyst. The catalyst used is said to be an organic tin compound. In this way a mixture of hydrocarbons results which can be separated, yielding a petrol fraction and heavier oils as well as gases. Some of the heavy oil is used for making the coal paste and other portions are further hydrogenated giving additional quantities of light oil on fractionation.

The gaseous product contains propane, butane and isobutane and is marketed under the name "Calor gas."

The Fischer-Tropsch process consists in passing water gas mixed with additional hydrogen over iron, cobalt or nickel catalysts at ordinary pressures and at a temperature between  $200^{\circ}$  and  $300^{\circ}$ . The "crude oil" so obtained can be fractionated as before: the nature of its constituents is determined to a considerable extent by the catalyst employed. This process has been extensively worked in Germany (e.g., at Leuna).

### § 19 Oxides of Carbon. Carbon Dioxide

Three oxides of carbon, all of which are gaseous at ordinary temperatures, are definitely known: carbon dioxide ( $\text{CO}_2$ ), carbon monoxide (CO), and carbon suboxide ( $\text{C}_3\text{O}_2$ ). Other oxides such as  $\text{C}_4\text{O}_3$ ,  $\text{C}_5\text{O}_2$ ,  $\text{C}_{12}\text{O}_9$  and  $\text{C}_8\text{O}_3$  have been reported but their existence has been disputed.

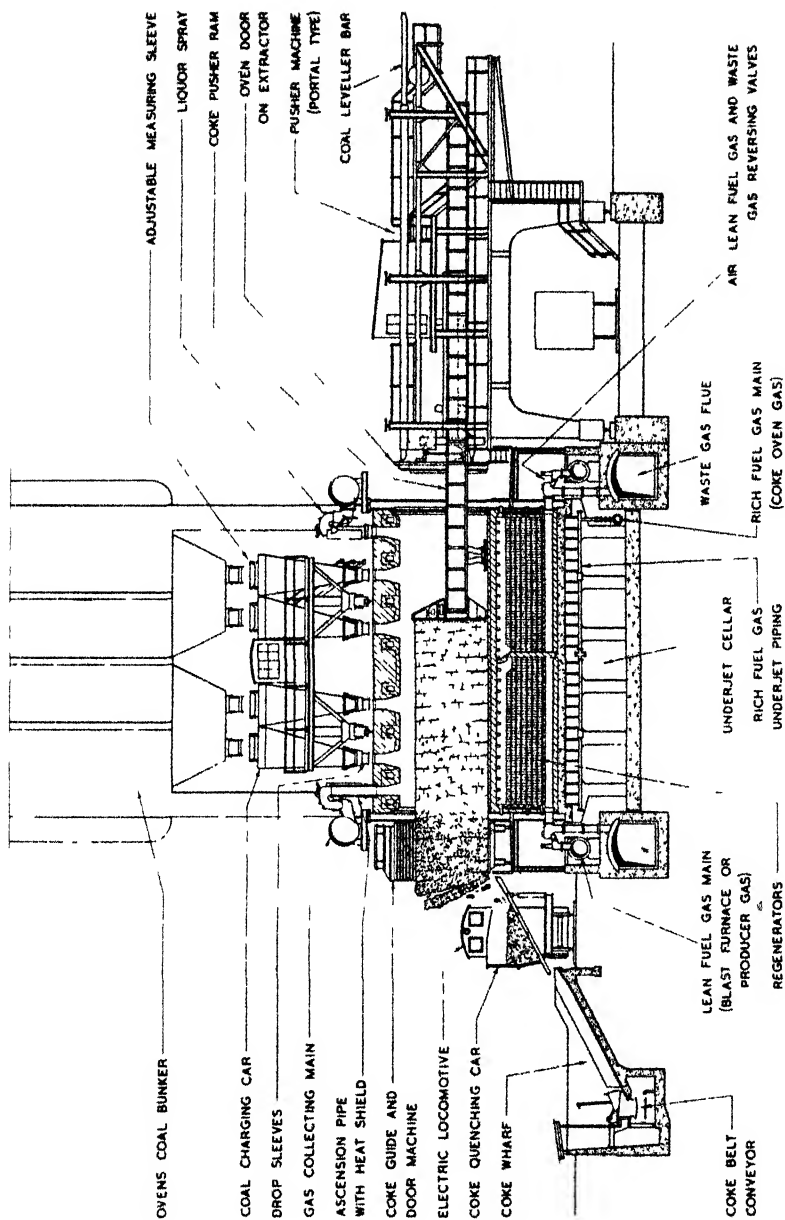


FIG. 22 10—Section of Regenerative Coke Oven  
(By courtesy of the Woodall-Duckham Construction Company Ltd.)

## Carbon Dioxide, $\text{CO}_2$

### History and Occurrence

Carbon dioxide has been known for a long time, but the early writers confused it with "air." J. B. van Helmont called it *gas sylvestre* to distinguish it from common air. He prepared it by the action of acids on alkalis and calcareous substances; he showed that it was formed during the combustion of charcoal, during the fermentation and the decay of organic matter, and he recognized it in the "mineral water" at Spa (Belgium); in the Grotta del Cane (Naples), and other localities. He also knew that the gas extinguished flame, and suffocated animals, but he confused it with other gases which do not support combustion. J. Black (1755), however, proved the gas to be a peculiar constituent of carbonated alkalis, being "fixed" there in the solid state. Hence Black called the gas *fixed air*; and T. Bergman (1774), *aerial acid*. The chemical nature of carbon dioxide was clearly explained by Lavoisier who showed it to be an oxide of carbon.

Carbon dioxide is present in the atmosphere to the extent of about 3 parts in 10,000 (0.03 per cent) by volume. This is a fact of the utmost importance and significance, for upon the presence of this carbon dioxide depends the continued existence of life as we know it. Both plants and animals consist essentially of carbon compounds; and the source of the carbon contained in them is ultimately the carbon dioxide in the atmosphere. Plants in sunlight are able to bring about what is known as *photosynthesis*, that is, they can build up sugars, starches, and other organic compounds from the carbon dioxide of the atmosphere and water. The carbon compounds contained in animals are derived either from plants eaten by the animals, or from eating other animals which in their turn have consumed plants as food.

The carbon thus absorbed by animals is ultimately partly returned to the atmosphere in the form of carbon dioxide exhaled by the lungs; while the decomposition of the dead bodies of plants and animals also liberates carbon dioxide. There is thus maintained a balance between plant and animal life which results in the maintenance of the proportion of carbon dioxide in the atmosphere at a remarkably steady value.

Carbon dioxide is appreciably soluble in water and a certain amount of carbon dioxide has been more or less permanently removed from the air through the formation by aquatic animals of shells composed of calcium carbonate. This is the origin of the enormous beds of limestone and chalk which exist in various parts of the world, and it is quite probable that this process is still going on. Against this may be set the fact that man is busily engaged in converting enormous quantities of coal and oil into carbon dioxide by burning them. These various changes are indicated diagrammatically by Fig. 22.11.

Carbon dioxide is found to issue from the ground in many places both as a gas and in aqueous solution (mineral water). J. B. Boussingault (1844) estimated that Cotopaxi emitted more carbon dioxide per

annum than was generated by life and combustion in a city like Paris. Owing to the fact that carbon dioxide is nearly one and a half times as dense as air, this gas is inclined to collect as a gas in old deep wells, in valleys, and in depressions in the ground near lime kilns; and in certain neighbourhoods where carbon dioxide is evolved from volcanoes and fissures in the ground—e.g., the Valley of Death (Lake of Laach, Java), where one traveller says the whole of the bottom is strewn with the skeletons of human beings, animals, and birds which have been asphyxiated in an atmosphere overloaded with carbon dioxide. In the Grotta del Cane (Pozzuoli, Naples) there is said to be a constant depth of about 18 inches of carbon dioxide on the floor so that dogs entering the cave are suffocated while men are safe.

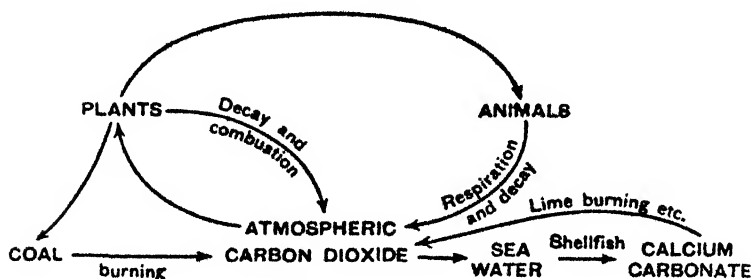


FIG 22 11 —Carbon Cycle

Carbon dioxide is also evolved in the Death Gulch in the Yellowstone Park and the skeletons of dead animals which have been suffocated by it are to be seen there.

### Production of Carbon Dioxide

Carbon dioxide is formed whenever carbon, or carbon compounds, are burned in excess of air, and this source of the gas is sometimes used, e.g., in the preparation of white lead (page 798). It can also be made:

- (i) by the action of heat on carbonates (except those of the alkali metals);
- (ii) by the action of acids on carbonates;
- (iii) by fermentation.

The first and third are common industrial sources of the gas, while the usual laboratory preparation is an example of the second.

### Preparation of Carbon Dioxide in the Laboratory

If a supply of carbon dioxide be required for experimental purposes it is now usually obtained from a cylinder of the liquid (cf. page 392). It is generally made in the laboratory by the action of dilute hydrochloric acid upon calcium carbonate—marble, limestone or chalk. The

operation may be carried out in a Woulfe's bottle or Kipp's apparatus (cf. Figs. 22.12 and 20.2, page 288). Fragments of marble are placed in the Woulfe's bottle and covered with water. Concentrated hydrochloric acid is added by way of the thistle funnel. The reaction is represented by the equation:

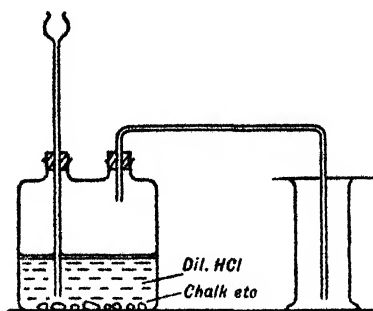
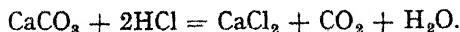


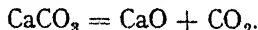
FIG. 22.12.  
Preparation of Carbon Dioxide

The gas is somewhat soluble in water and so it is usually collected by downward delivery as in Fig. 22.12. The gas can be dried by means of calcium chloride, or concentrated sulphuric acid, or phosphorus pentoxide.

It is not possible to use sulphuric acid in the preparation since the lumps of marble or limestone soon become covered with the very sparingly soluble calcium sulphate which then stops further action.

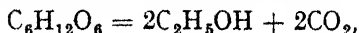
### Manufacture

Industrially, large quantities of carbon dioxide are obtained in the course of the manufacture of quicklime, which is made by the action of heat on limestone (see page 697). In the course of this operation, carbon dioxide is given off, and utilized:



This is the source of the carbon dioxide used in the Solvay process for the manufacture of sodium carbonate (see page 620).

In the brewing industry, large quantities of carbon dioxide are evolved as a result of the fermentation of sugars, or substances containing sugars, by yeast. The main reaction involved in the alcoholic fermentation of sugar may be represented by the equation:



but small quantities of several other substances are formed at the same time, so that there are probably a number of side reactions taking place also.

## § 20 Formula and Properties of Carbon Dioxide

### Formula

The composition of carbon dioxide can be determined directly both by weight and by volume. The composition by weight is found by burning a weighed amount of carbon—diamond, graphite, or sugar charcoal—at a red heat in a stream of oxygen, in an apparatus such as that indicated in Fig. 22.13.

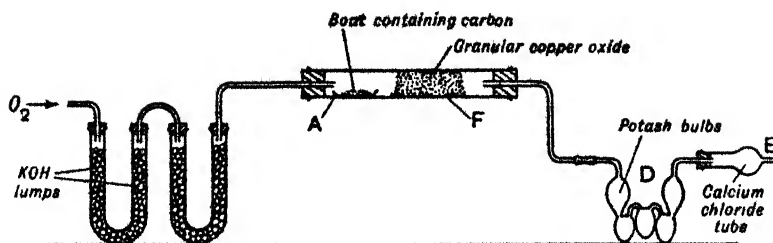


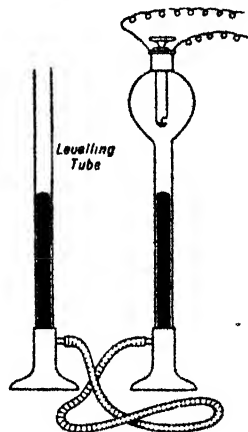
FIG. 22.13 —Gravimetric Composition of Carbon Dioxide

The carbon is weighed in a platinum or porcelain boat *A*, and placed in the hard glass tube, one half of which is packed with granular copper oxide *F*. The tube is heated by means of a combustion furnace, and a slow stream of pure, dry oxygen is passed through the apparatus. The carbon burns in the oxygen, and any traces of carbon monoxide which may be formed are completely oxidized to carbon dioxide by passage through the hot copper oxide *F*. The carbon dioxide is absorbed in the weighed potash bulbs *D*. The calcium chloride tube *E* is weighed along with the potash bulbs, as its purpose is to prevent loss of water vapour from *D* by being carried along by the stream of excess oxygen.

Experiments of this kind show that approximately 8 parts by weight of oxygen combine with 3 parts by weight of carbon; that is, the equivalent of carbon in this gas is 3. Since the vapour density of the gas is 22, its molecular weight is 44 and it follows that the weight of carbon in the molecular weight is  $\frac{3}{11}$  of 44; that is 12 units of weight which corresponds to one atom of carbon. Similarly the weight of oxygen is  $\frac{8}{11}$  of 44, that is 32, which corresponds to two atoms of oxygen. Therefore the formula of the gas is  $\text{CO}_2$ , which accounts for the name carbon dioxide.

The volumetric composition of carbon dioxide may be found in an apparatus such as that indicated in Fig. 22.14.

The bulb of the right tube, Fig. 22.14, is charged with oxygen; and the stopper, which carries a bone-ash crucible containing a chip of charcoal, is lowered into the position illustrated in the diagram. A slip of gummed paper is placed on the right tube indicating the position of the mercury when that liquid is at the same level in both tubes. The platinum wires are connected with the supply mains through a suitable resistance. The small loop of platinum wire in contact with the carbon is thus heated

FIG. 22.14.  
Composition of Carbon Dioxide by Volume

red hot. This ignites the carbon which burns to carbon dioxide. The heat of the combustion expands the gas, but in a short time, when the apparatus has cooled, the level of the mercury is the same as before the experiment. Hence the gas formed by burning carbon in excess of oxygen contains its own volume of oxygen.

The fact that carbon dioxide contains its own volume of oxygen indicates that its formula is  $C_nO_2$  for, by Avogadro's Law, it shows that one molecule of the gas contains one molecule of oxygen. Since the vapour density ( $H_2 = 1$ ) is found to be 22, its molecular weight is 44, and since it contains one molecule of oxygen, i.e., 32 units of weight, the amount of carbon is  $(44 - 32) = 12$  units of weight which corresponds to one atomic weight of carbon. The formula of the gas is therefore  $CO_2$ .

### Properties

Carbon dioxide is a colourless gas with a faint taste and smell. It is believed that it is not poisonous, and that its harmful effects are mainly due to suffocation (absence of oxygen), and to the physical disturbance of delicate equilibria. Small increases in the amount of carbon dioxide in air—say 2 or 3 per cent—do no perceptible harm; 5-6 per cent induces a rise of pulse and marked panting; 10 per cent violent panting; above this the gas exerts a narcotic effect, and with 25 per cent death will occur in a few hours; air with 50 per cent carbon dioxide can be breathed a short time without fatal results. The ill-effects which attend breathing in a badly ventilated room are probably due to the increase of moisture and temperature.

Water dissolves about  $1\frac{1}{4}$  times its volume of the gas at  $0^\circ$  and 760 mm. pressure; and about its own volume at  $15^\circ$ , 760 mm. In the manufacture of "soda water" the gas is dissolved by the water under pressure—60-150 lb. per square inch. The solution effervesces and froths when the pressure is released, owing to the escape of the carbon dioxide.

All natural waters contain dissolved carbon dioxide, and the existence and growth of aquatic plants depend upon its presence. The reaction of such waters with calcareous rocks has been referred to on page 308.

Carbon dioxide is comparatively easily liquefied, and it was first obtained in this state by Faraday in 1823 (page 46).

Liquid carbon dioxide is now manufactured as a commercial article by pumping the gas into steel cylinders (bombs) by powerful compression pumps. Liquid carbon dioxide is also utilized for making "home-made" soda water, the "sparklet" bulbs sold for this purpose being filled with it.

At  $-5^\circ$ , carbon dioxide requires a pressure of 30.8 atmospheres for liquefaction; at  $+5^\circ$ , 40.4 atmospheres; and at  $+15^\circ$ , 52.1 atmospheres; and over  $31.1^\circ$  it cannot be liquefied by any known pressure. Liquid carbon dioxide is a colourless mobile liquid. It floats on water without mixing with it. It boils at  $-78.5^\circ$  at atmospheric pressure.



If liquid carbon dioxide be allowed to escape into the air from the nozzle of the cylinder, the absorption of heat which attends the rapid evaporation causes a portion of the liquid to solidify. The solid is collected by tying a small canvas bag over the nozzle and inverting the cylinder. By opening the nozzle for a few minutes, quite a lot of solid carbon dioxide can be collected. The solid can be shaken from the bag into a cardboard box for examination. It crystallizes in the cubic system.

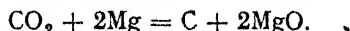
### Properties of Solid Carbon Dioxide

Solid carbon dioxide is a soft, white snow-like substance—"carbonic acid snow." It evaporates in air without melting, but under a pressure of 5 atmospheres it can be melted to a liquid. It can be handled safely provided no pressure is applied. The effect of pressure is to break the film of gas between the solid and the warm hand and cause a severe burn, or rather, a blister, resembling the blister produced by a burn. A horn spoon can be used for handling the material.

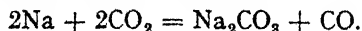
Solid carbon dioxide dissolves in ether, and as the ether evaporates, a temperature approaching  $-110^{\circ}$  can be obtained in air, and  $-140^{\circ}$  under reduced pressure. The solution is a good conductor for heat, and serves as an excellent freezing mixture. A great many gases can be liquefied by passing them through tubes immersed in this mixture.

Solid carbon dioxide is now a commercial product and is used as a refrigerant under the name of *Drikold*. It is convenient for this purpose since it leaves no residue. It is employed thus by itinerant ice-cream vendors and for the transport of perishable foodstuffs, e.g., by rail. Solid carbon dioxide is also used in the treatment of warts.

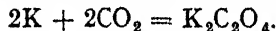
Chemically, carbon dioxide is a rather stable substance and it is not easily decomposed. It is denser than air, and extinguishes the flame of most burning bodies. It is non-combustible. Certain very active metals, e.g., sodium, potassium and magnesium, will, however, burn in carbon dioxide. With magnesium carbon is deposited in black specks:



This behaviour is possibly due to the high temperature causing slight dissociation of the carbon dioxide. Sodium when heated in a test-tube of carbon dioxide forms carbon monoxide:



Potassium at  $235^{\circ}$  yields some potassium oxalate:



Carbon dioxide is fairly stable at high temperatures. When heated under atmospheric pressure, at  $1300^{\circ}$ , only 0.004 per cent is decomposed; at  $1400^{\circ}$ , 0.14 per cent; and at  $1478^{\circ}$ , 0.32 per cent.

The solution of carbon dioxide in water exhibits feeble acid properties and is therefore believed to contain the acid carbonic acid,  $\text{H}_2\text{CO}_3$ .

carbon dioxide being consequently known as **carbonic anhydride**. Neither liquid nor dry gaseous carbon dioxide affects dry blue litmus paper, but if the paper be moistened it is coloured port-wine red. There can be little doubt, therefore, that in solution some of the gas forms carbonic acid by combination with the water:



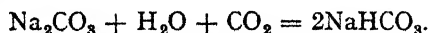
Carbonic acid is, however, unstable and has never been isolated; further, only a very small quantity of the acid is formed as is evident from the low solubility of the gas in water. The system is in equilibrium when but a small proportion of the dissolved gas has produced  $\text{H}_2\text{CO}_3$ . If a base be present, it will react with the carbonic acid and form a carbonate. More  $\text{H}_2\text{O}$  and  $\text{CO}_2$  unite, and the resulting  $\text{H}_2\text{CO}_3$  is removed by the base as fast as it is formed, until all the carbon dioxide in solution has been converted into carbonate.

**Orthocarbonic acid** corresponding with  $\text{C}(\text{OH})_4$ , or  $\text{H}_4\text{CO}_4$ , is not known, although some **orthocarbonates**, e.g., ethyl orthocarbonate,  $\text{C}(\text{OC}_2\text{H}_5)_4$ , are familiar to the student of organic chemistry. The ordinary "carbonates," now to be considered, are really **metacarbonates** derived from **metacarbonic acid**,  $\text{CO}(\text{OH})_2$ .

Carbonic acid is a di-basic acid (page 342) so that it forms two series of salts, **normal carbonates** and acid or **bicarbonates**. Thus, by the action of carbon dioxide on a solution of sodium hydroxide, there is first formed normal sodium carbonate:



but if excess of the gas be passed through the solution, sodium bicarbonate results:

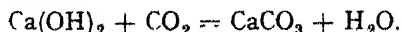


The analogous behaviour of slaked lime with carbon dioxide, which is of great importance in the study of hard water, has been discussed on page 308.

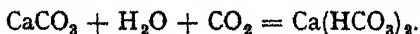
Solutions of caustic alkalis and slaked lime are thus excellent absorbers of carbon dioxide. In practice, potassium hydroxide is a better absorbent than sodium hydroxide since the sodium carbonate is less soluble than potassium carbonate and is liable to crystallize out and block the tubes of a wash-bottle or absorption apparatus.

### Detection and Determination

The action of the gas on lime water is the standard method for detecting carbon dioxide. Slaked lime (page 699) is only rather sparingly soluble, but calcium carbonate is virtually insoluble. If, therefore, a sample of lime water is brought into contact with carbon dioxide, calcium carbonate is precipitated, or, as it is commonly said, the lime water is "turned milky."



The action of excess of carbon dioxide causes the lime water to go clear again owing to the formation of the soluble bicarbonate (cf. page 308).



Carbon dioxide is determined by its action on baryta water (a solution of barium hydroxide—page 710). A known volume of the gas containing the carbon dioxide to be determined (e.g., air) is shaken up with, or aspirated through, a known volume of baryta water of known concentration (usually about N/50). Barium carbonate is precipitated and the excess of barium hydroxide is determined by titration with a standard solution of oxalic acid, using phenolphthalein as indicator. The determination in this way of the amount of carbon dioxide in the atmosphere is sometimes described as Pettenkofer's method.

### § 21 Uses of Carbon Dioxide

Carbon dioxide is employed in a variety of ways in industry. A familiar use, for which large quantities are required, is the making of soda water and aerated drinks. It is employed in fire extinguishers on account of its property of extinguishing flames. In some forms, these contain an acid contained in a glass bottle, and a bicarbonate (usually sulphuric acid and sodium bicarbonate). The extinguisher is brought into operation by a blow on a plunger so placed as to break the bottle. When the two substances mix, carbon dioxide is evolved and may be used to project a stream of water highly charged with carbon dioxide on to the fire. The foam type of fire extinguisher depends upon the formation of a stable foam of carbon dioxide bubbles, by mixing the water with a substance such as glue or alum which reduces its surface tension considerably.

Cylinders of the liquid are used as a source of carbon dioxide for inflating collapsible life-rafts and the gas is also employed in medicine as a respiratory stimulant.

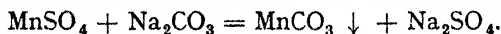
The use of liquid carbon dioxide in the steel industry for hardening steel has been tried, particularly by the firm of Krupp. If liquid carbon dioxide is allowed to come into contact with molten steel in strong gas-tight chambers, a very high pressure of gas results which frees the casting from bubbles. Carbon dioxide is also used for precipitating lime in the manufacture of sugar; in the Solvay process for the manufacture of sodium carbonate (page 620); and directly or indirectly in the production of white lead. There has also been much work done recently on the preservation of fruit in an atmosphere of carbon dioxide. This is being applied particularly to the storage of apples. Similarly it is used in the transport of "chilled" meat, which has been found to travel satisfactorily in an atmosphere containing the right proportion of carbon dioxide. It has also found application in the destruction of insects in grain silos. The use of solid carbon dioxide as a refrigerant has been mentioned earlier. Further uses of the solid

are the shrinking of metal parts to form close unions (the converse of the usual tyre-shrinking process) where heat would have an adverse effect on the properties of the metal, and to prevent premature "ageing" of certain aluminium alloys, particularly rivets used in the construction of aircraft. The solid is also used to freeze locally the contents of a pipe-line when the flow has to be stopped for repairs.

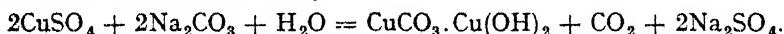
## § 22 Carbonates

Most metals form carbonates and a great many of these are found native. The only important metals which do not form carbonates are those whose hydroxides are very weak bases, for example, chromium.

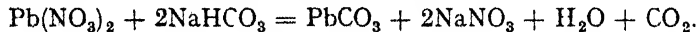
Metallic carbonates are usually insoluble; those of the alkali metals being the only important exceptions. They can usually be prepared, therefore, by precipitation by the action of a solution of sodium carbonate, or bicarbonate, on a solution of a soluble salt of the metal, e.g.,



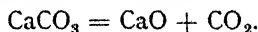
In many instances the use of sodium carbonate results in the formation of a *basic* carbonate, e.g.,



It is sometimes possible in such cases to obtain the normal carbonate by using sodium *bicarbonate* solution, e.g.,

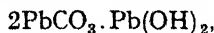


All carbonates, except those of the alkali metals, decompose on heating with evolution of carbon dioxide and formation of the oxide of the metal, e.g., "lime-burning," page 697.



Carbonates are decomposed by acids with evolution of carbon dioxide. The action of excess of carbon dioxide on carbonates results in the formation of bicarbonates, but with the exception of those of the alkali metals they cannot, as a rule, be isolated.

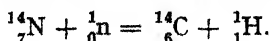
Many basic carbonates are known, some of which are of importance, as, for example, white lead, which is usually given the formula



although it is not certain that it is a definite compound. (Cf. page 798.)

## § 23 Radio-carbon Dating

The carbon dioxide of the atmosphere contains a trace of the carbon-14 isotope. This isotope is radioactive, emitting  $\beta$ -particles, and results from the action of neutrons on the nitrogen of the air



The neutrons are produced by cosmic rays. The carbon dioxide is in biological equilibrium with the carbon of living organisms which thus, while living, contain a very small, but yet definite, proportion of carbon-14. After the death of the organism, biological exchange with the carbon dioxide of the atmosphere ceases so that the carbon-14 content diminishes exponentially at a rate determined by the known half-life of the isotope (5300 years). It is thus possible to fix the "age" of materials of organic origin, such as wood, by measuring its residual radioactivity.

These measurements are difficult to make accurately because the radioactivity is very feeble but, nevertheless, the method has been developed in connection with the study of archaeology. The radioactivity of organic materials older than about 40,000 years is too faint to be measured accurately, so that it is not possible to determine the age of coals in this way. But, on account of the virtual inactivity of geological specimens it is possible to distinguish between natural and synthetic organic compounds (e.g., acetic acid).

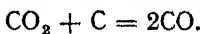
## § 24 Carbon Monoxide, CO

### Occurrence

Carbon monoxide seldom occurs free in nature, and then only in small quantities. Minute traces have been detected in air, in volcanic gases, occluded in coal, and in meteorites. It is found in tobacco smoke, in chimney gases where the air is not in a sufficiently large excess, in the gases from blast and other furnaces, and in the exhaust gases of internal combustion engines. It is an important constituent of fuel gases such as town gas (page 383), producer gas (page 399) and water gas (page 400).

### Preparation

Industrially, carbon monoxide is made in large quantities in the form of producer gas and water gas, as described below (pages 399–401). It can be prepared in the laboratory by the action of concentrated sulphuric acid either on formic acid or oxalic acid (whereby the elements of water are removed); or on ferrocyanides. Carbon monoxide is also formed by passing carbon dioxide over strongly heated carbon, but the process is not easy to carry out in the laboratory.



The method usually employed in the laboratory is the action of concentrated sulphuric acid on formic acid.

A suitable quantity (say 200 c.c.) of concentrated sulphuric acid is placed in a 500 c.c. flask, fitted with a tap funnel and delivery tube as in Fig. 22.15. The flask is heated and formic acid dropped on to the sulphuric acid from the tap funnel. The gas evolved is washed with sodium hydroxide solution, to remove traces of carbon dioxide and

sulphur dioxide, and collected over water. It can be dried by means of the usual drying agents, as, for example, calcium chloride, concentrated sulphuric acid or phosphorus pentoxide. The reaction taking place is the withdrawal of the elements of water by the sulphuric acid:

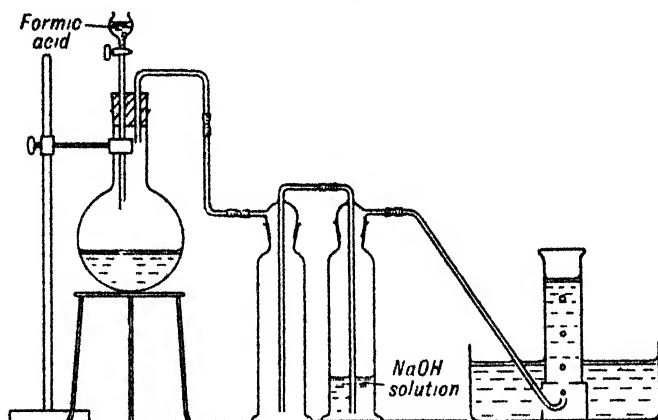
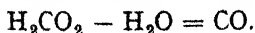
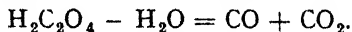
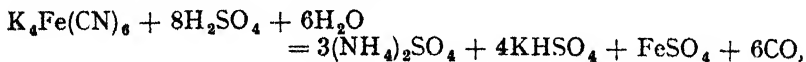


FIG 22 15 — Preparation of Carbon Monoxide

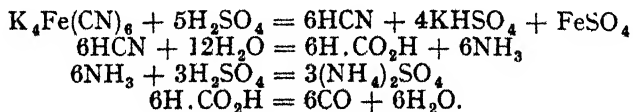
If oxalic acid is used it is desirable to use a second wash-bottle containing sodium hydroxide solution since the volume of carbon dioxide formed is equal to that of the carbon monoxide:



Carbon monoxide is also sometimes prepared by heating potassium ferrocyanide (page 925) with 10–20 times its weight of concentrated sulphuric acid, but a rather high temperature is required. The reaction is usually represented by the equation



but it is probable that it takes place in stages. Hydrocyanic acid is thought to be first formed, and then hydrolysed to formic acid and ammonia. The former is then dehydrated by the sulphuric acid as above:

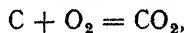


Summarized, these four equations reduce to the one given above.

### § 25 Producer Gas

Producer gas consists of a mixture of carbon monoxide and nitrogen, formed when air is blown through incandescent coke. Producer gas thus obtained is cheap, but since its calorific value is not very high, distribution would be uneconomic. It is usually made, therefore, *in situ*, as when required for heating the retorts in gas-works (page 378). The apparatus in which this gas is made is called a **producer**, and is illustrated diagrammatically by Fig. 22.16.

The producer consists essentially of a large air-tight, cylindrical furnace made of sheet iron lined with firebrick, provided with an orifice at the base through which air can be blown, and an outlet for the producer gas at the top. Devices are provided to enable fresh coke to be added at the top and ash to be removed at the bottom, without admission of unwanted air. The producer is filled with coke (which rests on firebars at the bottom) and air is forced through the hot fuel. The air, when it first enters the producer, probably oxidizes some coke to carbon dioxide:



which passes farther up the furnace, where it is reduced to carbon monoxide by the excess of red-hot coke:



There thus passes out of the producer a gas consisting essentially of carbon monoxide with nitrogen from the air used.

There is, in fact, an equilibrium set up in the producer between carbon dioxide and carbon monoxide, as indicated by the last equation.

The relative proportion of carbon dioxide to carbon monoxide, for equilibrium, is determined by the temperature. For instance, any mixture of carbon monoxide and carbon dioxide when heated in the presence of carbon produces at:

Temperature	Per cent by volume	
	CO	CO <sub>2</sub>
450°	2	98
750°	76	24
1050°	99.6	0.4

This shows that if the temperature of a producer be in the vicinity of 450°, very little combustible gas will be obtained; and conversely,

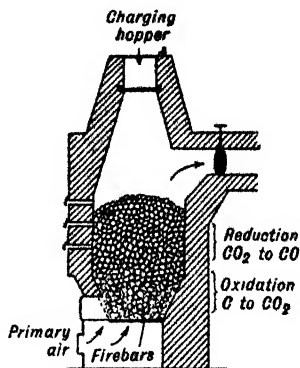


FIG. 22.16. —Gas Producer

in the vicinity of  $1000^{\circ}$ , nearly the maximum possible amount of combustible carbon monoxide will be present. Hence the temperature of the producer should be about  $1000^{\circ}$  in order to get the maximum yield of carbon monoxide with a minimum loss of heat.

A considerable amount of heat is liberated in the producer, and so the gas comes off at a high temperature. The gas, therefore, should not be allowed to cool before being used, or this heat will be wasted. This is an additional important reason for the production of producer gas *in situ*.

When producer gas is used for heating a retort bench or furnace, the bed of the latter consists of two parts, viz., the producer proper and a combustion chamber. In the former air is admitted in such amount as will form producer gas (this is known as the *primary air*); while in the combustion chamber what is called *secondary air* is admitted in suitable quantity so that the carbon monoxide burns to carbon dioxide. An example of this is furnished by the furnace employed for heating the retorts in the gasworks (page 378).

### § 26 Water Gas

When a current of steam is blown through a bed of hot carbon (say in a gas producer), the two interact, forming hydrogen and carbon monoxide:



The resulting mixture has a very high calorific power and it is called **water gas**. Water gas is almost free from diluting nitrogen. If the reaction occurs below  $1000^{\circ}$ , carbon dioxide begins to accumulate in the gas, and this the more the lower the temperature of the reaction.

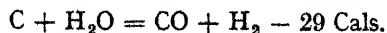
The following table (XXXI), due to Bunte, shows the proportions of the gases formed at various temperatures.

TABLE XXXI.—EFFECT OF TEMPERATURE ON FORMATION ON THE COMPOSITION OF WATER GAS

Temperature	Per cent of steam decomposed	Percentage composition of gas produced		
		Hydrogen	Carbon monoxide	Carbon dioxide
$674^{\circ}$	8.8	65.2	4.9	29.8
$1010^{\circ}$	94.0	48.8	49.7	1.5
$1125^{\circ}$	99.4	50.9	48.5	0.6

As was the case in the manufacture of producer gas, it is necessary here also that the temperature of the coke should not fall below  $1000^{\circ}$ .

The reaction which forms water gas proceeds with absorption of heat, that is, it is an endothermic reaction (page 239), as is shown by the equation:





Hence, it follows that when steam is blown over incandescent coke in order to make water gas, the temperature of the fuel will fall. It is, therefore, necessary to provide heat from another source in order to maintain the temperature of the producer sufficiently high to prevent undue amounts of carbon dioxide accumulating in the products of the reaction. In modern water-gas plants, the carbon in the producer is raised to incandescence by a blast of air—the *air blow*—continued for about two minutes. This is followed by a jet of steam until the temperature falls to dull redness—*steam blow*—continued for about four minutes. When the air blow is in progress, the producer is not making water gas, and, in consequence, a damper is used to deflect the stream of gas from the producer elsewhere.

The two operations described above are sometimes combined and just enough air is mixed with the steam to keep the fuel hot. The resulting gas contains nitrogen and a larger proportion of carbon monoxide than water gas, and is known as **semi-water gas**.

Water gas burns with a non-luminous flame, and, though a valuable heating agent, it is useless for lighting purposes unless it be employed in conjunction with, say, an incandescent mantle. Hence, if water gas is to be used as an illuminating agent, it is charged with hydrocarbon gases which do not condense on cooling. The mixture is called *carburetted or enriched water gas*. The carburetting is conducted as follows: When the air blast is in progress, the products of combustion from the top of the producer are deflected down a tower containing chequered brickwork, and called the *carburetter*; then up another tower also containing chequered brickwork, called the *superheater*; and thence into the air. The result of this is to raise the temperature of both towers—the carburetter and the superheater. The air valve at the top of the superheater is deflected so that the superheater is put in communication with a third tower resembling the *scrubber* of a gas works. A spray of oil is simultaneously directed into the top of the carburetter, and steam is blown into the producer. As the water gas and oil pass down the hot carburetter, the oil is decomposed—"cracked"—and the decomposition is completed in the superheater. In this way, the oil is transformed into gases which do not liquefy when cooled. The gas is purified and washed in the scrubber, and thence passed to the gasholder.

## § 27 Formula and Properties of Carbon Monoxide

### Formula

In § 20 (page 391) it has been shown that carbon dioxide contains its own volume of oxygen. By means of an eudiometer experiment, it can be shown that two volumes of carbon monoxide will unite with one volume of oxygen to form two volumes of carbon dioxide. Hence, by Avogadro's hypothesis, two molecules of carbon monoxide and one molecule of oxygen give two molecules of carbon dioxide. The formula

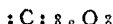
of the latter being  $\text{CO}_2$ , that of the former is therefore  $\text{CO}$ . This is confirmed by the vapour density, which is 14 ( $H_2 = 1$ ).

In the vast majority of its compounds carbon is found to be quadrivalent; but it cannot be so in carbon monoxide unless oxygen is also quadrivalent. In consequence it was formerly assumed that in carbon monoxide the carbon is divalent with two "sleeping" valencies. This is in agreement with the readiness with which carbon monoxide can form addition compounds (see below).

The interpretation of this conclusion in terms of the electronic theory of valency (Chapter 11) has given rise to controversy, since the formula  $\text{C} = \text{O}$ , translated into terms of electrons, etc., becomes:



A compound of this structure would, however, have a large dipole moment (page 157), whereas experiment shows that carbon monoxide has a very small dipole moment. This has been explained by the formula  $\text{C} \equiv \text{O}$ , which, in terms of electrons, becomes:



This is supported by the fact that in the known addition compounds of carbon monoxide, it behaves as a *donor* but not as an *acceptor*. Thus, it does not combine with water or ammonia, while it forms addition compounds with chlorine, and many metals, such as nickel. Also the physical properties of carbon monoxide resemble those of nitrogen and this structure is also similar to the structure of nitrogen,  $\text{N} = \text{N}$ , or



### Properties

Carbon monoxide is a colourless, tasteless, and odourless, poisonous gas. One volume of water dissolves 0.035 volume at  $0^\circ$ , and 0.023 volume at  $20^\circ$ . The gas condenses to a colourless transparent liquid at  $-192^\circ$ , at atmospheric pressure; the liquid solidifies at  $-207^\circ$ . When a lighted taper is plunged into the gas, the taper is extinguished (non-supporter of combustion), but the gas is inflamed (combustible), and burns with a blue flame. The blue lambent flame which appears on the surface of a clear red coke (or coal) fire, or over the ignited lime in a lime kiln, is carbon monoxide.

On burning in air or oxygen carbon dioxide is formed:

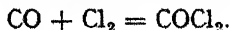


Mixtures of air or oxygen with carbon monoxide are highly explosive in the ordinary way; but the explosion does not occur easily if the mixture is absolutely dry. This was the first well-investigated case of the effect of intensive drying (see page 317).

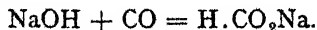
Carbon monoxide is a stable gas and is not decomposed by rise of temperature. It is generally regarded as a neutral oxide, although it combines with sodium hydroxide when heated with it under pressure.

Carbon monoxide readily forms addition products. The formation of carbon dioxide when it burns in air is an example of this. Thus it will combine with chlorine, when a mixture of the two gases is exposed

to light, particularly in the presence of charcoal, forming **phosgene** or **carbonyl chloride**:



Similarly, a mixture of carbon monoxide and sulphur vapour when passed through a hot tube forms carbonyl sulphide, COS, a reaction analogous to the formation of carbon dioxide, when it burns. Again when heated to 200° with solid caustic soda at 6 to 10 atmospheres, *sodium formate* results:



This reaction is now used commercially. Carbon monoxide also forms an addition product with cuprous chloride, and hence solutions of this salt in hydrochloric acid or ammonia can be used as absorbents for the gas. Carbon monoxide also forms interesting compounds, known as carbonyls, with certain metals (particularly some of those in Group VIII of the Periodic Table). *Nickel carbonyl* is employed in the extraction of nickel from its ores (page 934).

Carbon monoxide is an important reducing agent, and when passed over the heated oxides of many metals reduces them to the metals themselves. It plays an essential part in the production of iron in the blast furnace (page 901).

Carbon monoxide is an active poison. When it is respired in the lungs, it unites with the haemoglobin of the blood, forming a bright cherry-red coloured compound, carbonyl haemoglobin, which prevents the haemoglobin performing its regular work of oxidizing waste tissue. Less than 1 per cent in the atmosphere is sufficient to cause death when inhaled. J. S. Haldane says that air containing  $\frac{1}{20}$  of 1 per cent of carbon monoxide will produce giddiness on exertion if breathed for from one-half to two hours; and  $\frac{1}{10}$  of 1 per cent makes one unable to walk;  $\frac{1}{5}$  of 1 per cent leads to loss of consciousness and perhaps death;  $\frac{4}{5}$  of 1 per cent means probable death; and 1 per cent will lead to unconsciousness in a few minutes, followed before long by death. Fatal accidents have arisen from the breathing of carbon monoxide when its presence has not been suspected. It is formed when a gas flame is exposed to a cold surface as might occur in some "patent water heaters" used in ill-ventilated bathrooms, etc.; in slow combustion stoves, and charcoal pans. It is often present in places where gas producers are at work; and in rooms with an escape of coal gas. The poisonous character of "after-damp" in coal mines is owing to the presence of some carbon monoxide along with the carbon dioxide formed during an explosion of firedamp or coal dust; in air after the use of explosives for blasting; underground fires, etc. The exhaust gases from petrol-driven motor-cars contain a substantial proportion of carbon monoxide. It is, therefore, very dangerous to run the engine of a car in a closed garage.

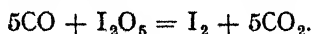
Carbon monoxide can be absorbed by respirators containing a mixture of manganese dioxide (50 per cent.), copper oxide (30 per cent.),

cobaltic oxide (15 per cent), and silver oxide (5 per cent), known as *hopcalite*. This catalyses the oxidation of the carbon monoxide by the oxygen of the air at ordinary temperature.

### § 28 Detection and Determination of Carbon Monoxide

The detection of carbon monoxide is not easy. (1) A piece of white filter paper moistened with a solution of *palladous chloride* is turned pink, green, or black, owing to the reduction of the chloride to the metal. The intensity of the tint is proportional to the amount of carbon monoxide in the given atmosphere (freed from ammonia and hydrogen sulphide).

(2) Iodine pentoxide is reduced by carbon monoxide at 90°:



This reaction can be used for the determination of carbon monoxide, and it is a sensitive test for the gas. The liberated iodine gives a violet solution with chloroform or carbon disulphide, or it can be absorbed in potassium iodide solution. (Cf. page 570.)

(3) *Vogel's blood test* is considered the most reliable. If ordinary blood be diluted with 200 times its volume of water, a yellowish-red solution is obtained; with blood containing carbon monoxide the solution is distinctly pink.

The spectrum of haemoglobin in normal blood shows two absorption bands, which disappear on the addition of ammonium sulphide, and a single band is seen in between these positions. Blood containing carbonyl haemoglobin gives a very similar spectrum to haemoglobin itself, but ammonium sulphide does not cause any marked change. Hence, if a sample of diluted blood is treated with air suspected of containing carbon monoxide, followed by addition of ammonium sulphide, the presence of *two* absorption bands is evidence of the presence of carbon monoxide.

In ordinary gas analysis, the proportion of carbon monoxide in a mixture may be determined by first removing acid gases such as carbon dioxide by means of a solution of sodium hydroxide, and then absorbing the carbon monoxide in ammoniacal cuprous chloride solution.

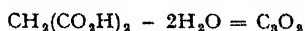
### § 29 Uses of Carbon Monoxide

Carbon monoxide, usually either in the form of producer gas or water gas, has many technical applications. One of the most important is in the extraction of metallic nickel from its ores, where its use depends upon the formation and subsequent decomposition of nickel carbonyl (page 403). It is employed in the manufacture of formates (and hence oxalates), by action on sodium hydroxide under pressure. When mixed with hydrogen (in the form of water gas) it readily forms methane by passage over nickel at a temperature of about 300°.

This process has been employed on a large scale for the production, from water gas, of a gas of high calorific power and some illuminating properties also. It has even been suggested that the carbon monoxide present in modern town gas should be converted into methane in this way, thus making it much less poisonous and increasing its calorific value. By passing a similar mixture at 200 atmospheres pressure over a catalyst consisting of zinc and chromium oxides, at a temperature of  $350^{\circ}$ – $400^{\circ}$ , methyl alcohol is made in quantity; and by modifying the catalyst (e.g., by using an alkalized iron catalyst) higher alcohols and other organic compounds containing up to nine carbon atoms can be obtained. This mixture of products is marketed under the name *synthol*. Carbon monoxide is used also for the manufacture of phosgene which is used in the dye industry, and also found a use—or abuse—in chemical warfare. Its employment as a reducing agent in metallurgy has already been mentioned; this use is being extended in some quarters to the reduction of organic compounds. The use of carbon monoxide as a fuel is, of course, of great importance and wide application.

### § 30 Carbon Suboxide, $C_3O_2$

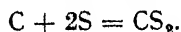
This is made by the action of phosphorus pentoxide on malonic acid:



Carbon suboxide is a colourless gas, of suffocating odour, which condenses to a liquid at  $6^{\circ}$ , and decomposes when warmed. It burns with a blue, smoky flame, forming carbon dioxide. With water it regenerates malonic acid, so that it may be regarded as malonic anhydride.

### § 31 Carbon Disulphide, $CS_2$

Carbon disulphide was discovered by W. A. Lampadius in 1796 while studying the action of pyrites on carbon. Clément and Désormes rediscovered it in 1802. It is formed when sulphur vapour is passed over red-hot carbon, in the form of charcoal or coke:



It is not easy to prepare in the laboratory, but is an important article of commerce.

In the manufacturing process (Zahn's) the sulphur is melted and then run into a preheater (Fig. 22.17) which is cast integrally with the retort proper. The sulphur is thus vaporized and passed into the retort which

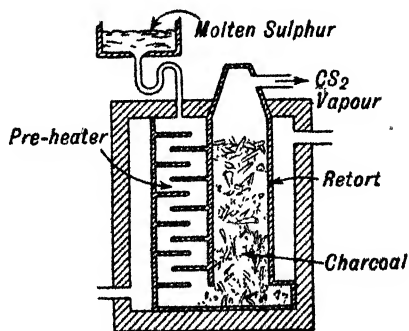


FIG. 22 17.—Zahn's Process

contains charcoal heated to 900°. The carbon disulphide is condensed in long condensing coils and purified by fractional distillation.

In Taylor's electric process (1899) a cylindrical furnace 40 ft. high and 16 ft. in diameter is packed with coke from the top, Fig. 22.18; the coke is renewed through the side hopper *C*. An alternating current is sent through the electrodes *E* set at right angles to one another at the base of the furnace. The heat melts the sulphur on the floor of the

furnace; the vapour of sulphur rises through the coke, forming carbon disulphide. Fresh sulphur is introduced through the hopper as shown in the diagram. The carbon disulphide passes off at the top of the furnace, and is condensed in condensing coils.

A newer process involves the reaction of hydrocarbons, such as methane, or natural gas, with sulphur vapour in presence of a catalyst at 500°–700°.



Silica gel can be used as the catalyst and the sulphur in the hydrogen sulphide is recovered by the Claus process.

Carbon disulphide, if pure, is a colourless, mobile, refractive liquid, with an aromatic smell not at all displeasing, although the smell of commercial carbon disulphide is usually disagreeable and rancid.

Light slowly decomposes the pure liquid in such a way that a small quantity of some product—possibly a polymer—is formed which raises the boiling point of the liquid and produces an unpleasant smell. Air also seems to affect it, particularly if the temperature is raised a little. So sensitive is purified carbon disulphide to these influences that it has been said: pure carbon disulphide is an ephemeral product. If breathed constantly, in small quantities, carbon disulphide is injurious to health, and in large quantities, fatal. Its specific gravity at 0° is 1.292. It freezes at –111°; and boils at 46.3°. 100 grams of water at 0° dissolve 0.242 gram of carbon disulphide; and at 20°, 0.210 gram. Most of the alkali salts are insoluble in carbon disulphide; several salts of other metals are sparingly soluble in this liquid. Carbon disulphide is extremely inflammable and as it ignites at a very low temperature (a hot rod is sufficient to ignite it) it is a very dangerous substance and must be handled with great care. The vapour forms an

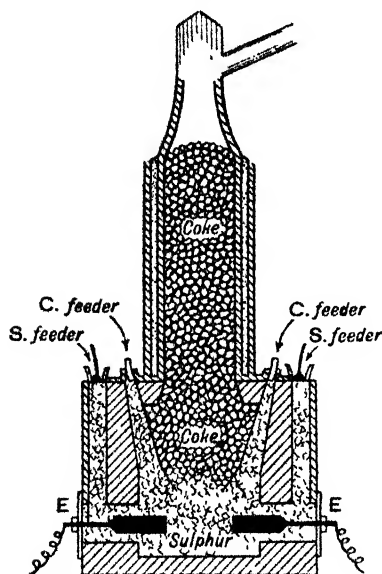
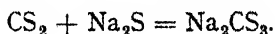


FIG. 22 18 —Taylor's Carbon Disulphide Furnace

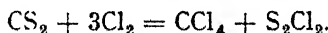
explosive mixture with air or oxygen. Carbon disulphide mixes in all proportions with alcohol, ether, benzene, and essential oils. It is also a good solvent for sulphur, phosphorus, iodine, bromine, camphor, gums, resins, waxes, fats, and caoutchouc; and it is largely employed in the industries on account of its solvent properties. It is also used as an insecticide. A very important use now is in the manufacture of artificial silk by the *viscose* process for which large quantities are used.

Carbon disulphide reacts under suitable conditions with chlorine to form carbon tetrachloride and sulphur chloride (see below). It also reacts with alkali sulphides, giving substances known as **thiocarbonates** on account of their analogy with the carbonates.



### § 32 Carbon Tetrachloride, $\text{CCl}_4$

Carbon tetrachloride is made by the action of chlorine on carbon disulphide containing a little iodine or aluminium chloride in suspension:



The carbon tetrachloride can be separated from the sulphur chloride by distillation. It is purified by washing with dilute sodium hydroxide, and redistillation from bleaching powder.

Carbon tetrachloride is rather important commercially as a solvent for fats—degreasing woollen and linen fabrics, bones, oleaginous seeds, etc. It can replace benzene, which is dangerously inflammable. Carbon tetrachloride is a colourless non-inflammable liquid of specific gravity 1.63, boiling at  $76.7^\circ$ .

Carbon tetrachloride is remarkable in that, being the chloride of a non-metal, it is not readily decomposed by water. Its behaviour in this respect may be compared with that of boron trichloride (page 742), silicon tetrachloride (page 781) and phosphorus trichloride (page 831), all of which are decomposed by cold water. This behaviour is accounted for by the fact that, for elements in the first short period of the Periodic Table, the *co-valency maximum* is four. Boron trichloride, silicon tetrachloride and phosphorus trichloride can form transient addition compounds with water; boron trichloride has only a sextet of electrons in the valency group and silicon tetrachloride (and the halides of phosphorus) can form a temporary addition compound by expanding this group to twelve. Carbon not only has a complete octet but having a relatively small atom it cannot expand further. When heated with water, especially in presence of iron or copper, carbon tetrachloride is attacked, yielding phosgene (carbonyl chloride):



In these conditions it attacks metals owing to the formation of hydrochloric acid.

Carbon tetrachloride is used extensively in the dry-cleaning industry, where it is preferred to hydrocarbon solvents on account of its non-inflammability. It is used also in fire extinguishers (e.g., under the name *Pyrene*); the heavy vapour blankets the fire by excluding the air.

### § 33 Cyanogen and its Compounds

There is a considerable group of compounds, containing the —CN or —NC radical, which are of importance, particularly from the viewpoint of organic chemistry. Certain of them are properly considered in inorganic chemistry. The radical —CN itself shows some resemblance in its reactions to a chlorine atom, and was one of the first radicals, whose behaviour as a group resembles that of a single atom, to be clearly recognized.

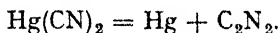
#### Cyanogen, $C_2N_2$

Cyanogen was first isolated by Gay-Lussac in 1815 by the action of heat on silver cyanide.

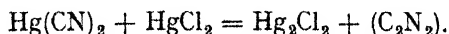
Morren (1859) and Berthelot (1879) showed that cyanogen can be obtained directly from its elements by sparking carbon electrodes in nitrogen gas; and cyanides are formed, as indicated on page 424, by heating the two elements in contact with a metal—preferably of the alkalis or alkaline earths. The endothermic reaction is symbolized:



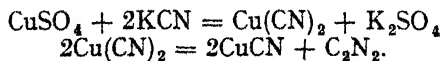
Cyanogen is a gas made by heating mercuric or silver cyanide in a hard glass tube; mercuric cyanide is, on the whole, more convenient:



The gas can be collected over water, but it is somewhat soluble and so is best collected over mercury. The yield of cyanogen is much less than the theoretical owing to the formation of a dark brown powder called **paracyanogen**. This substance appears to be a polymer of cyanogen  $(CN)_n$ , because, if heated to about  $850^\circ$ , it gives ordinary cyanogen. If the mercuric cyanide be mixed with mercuric chloride, the cyanogen comes off at a lower temperature, and less paracyanogen is formed:



A convenient method for the preparation of cyanogen (though it is liable when prepared thus to contain traces of carbon dioxide and hydrocyanic acid) is to add a solution of potassium cyanide to a warm solution of copper sulphate. Cupric cyanide,  $Cu(CN)_2$ , is first formed as a yellow precipitate, but it at once decomposes into cuprous cyanide,  $CuCN$ , and free cyanogen:





This reaction closely resembles that between copper sulphate and potassium iodide (page 658).

Cyanogen is a colourless poisonous gas with a faint odour which reminds some people of the smell of peaches. Cyanogen burns with a pink-tinged flame, forming carbon dioxide and nitrogen. It condenses to a liquid under a pressure of four atmospheres at ordinary temperatures, and at ordinary pressures it furnishes a liquid boiling at  $-20.5^{\circ}$ . The liquid freezes to a white solid melting at  $-34.4^{\circ}$ . The gas has a vapour density of 26 ( $H_2 = 1$ ), which corresponds with the molecule  $C_2N_2$ . The molecule of cyanogen is linear and is represented by the formula  $N \equiv C - C \equiv N$ . Cyanogen dissolves readily in water. The aqueous solution deposits a peculiar brown flocculent mass—**azulmic acid**—on standing; ammonium oxalate, hydrogen cyanide, and carbon dioxide are formed at the same time. Cyanogen unites directly with the alkali metals, forming cyanides.

When passed into a solution of potassium hydroxide, potassium cyanide and potassium cyanate are formed:



a reaction analogous to that of chlorine (page 547).

### § 34 Hydrocyanic Acid, HCN

K. W. Scheele discovered hydrocyanic acid in 1782; and made it by heating sulphuric acid with Prussian blue, hence the old name, *prussic acid*; and I. von Ittner made the anhydrous compound, HCN, in 1809. J. L. Gay-Lussac established its composition in 1811.

It is found in nature combined with the sugar glucose and another organic compound, benzaldehyde, as the glucoside *amygdalin* which is found in bitter almonds and other plants.

Hydrogen cyanide is made by distilling a mixture of powdered potassium cyanide with a mixture of equal volumes of sulphuric acid and water; if concentrated acid be used, a considerable amount of carbon monoxide is evolved. The vapour is passed through a U-tube containing calcium chloride to remove the water. The dry hydrogen cyanide is led through a U-tube surrounded by ice; and the gas condenses to a colourless liquid. The gas is also made by passing dry hydrogen sulphide over dry mercuric cyanide and condensing the vapour to a liquid as before. Pure hydrogen cyanide is one of the most deadly poisons known, and hence great care must be taken in experiments with hydrogen cyanide, and, indeed, with cyanides generally. The liquid boils at  $26^{\circ}$ , and freezes at  $-14^{\circ}$  to a white solid. It dissolves in water in all proportions, and the solution has the smell familiarly associated with sweet almonds. The anhydrous acid is a colourless liquid. It is a very weak acid indeed, and so its salts are strongly hydrolysed in aqueous solution. It is used in the fumigation of ships to destroy rats and vermin, and for spraying fruit trees.

Being an acid, it forms salts which are known as **cyanides**; the most important of these are sodium and potassium cyanides which are much used in industry (see page 634). The cyanides of other metals are usually made by double decomposition with potassium cyanide.

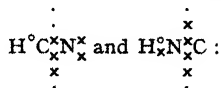
Metallic cyanides are noteworthy for their tendency to form complex ions. Some of these, notably the ferrocyanides (see page 924), are very stable, while others are less so. The ferrocyanides of copper and iron are of interest and importance (see pages 200 and 924); while the use of potassium cyanide in the extraction of silver and gold from their ores depends also upon the formation of complex ions with silver and gold cyanides.

Hydrocyanic acid and the cyanides can be formulated either as  $\text{H}-\text{C}\equiv\text{N}$  where the hydrogen is attached to carbon or as  $\text{H}-\text{N}\equiv\text{C}$  where the hydrogen is attached to nitrogen, and organic derivatives of both are known. The exact formulation of the latter form has given rise to controversy in the past; it is now believed to be as shown, that is, analogous to carbon monoxide.

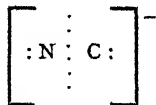
The acid itself is thought to be an equilibrium mixture:



with the former predominating. The corresponding electronic formulae being



the cyanide ion is identical from whichever form it is derived, viz.:



which is in accordance with the chemical behaviour of cyanides in solution.

### § 35 Cyanic Acid and Cyanates

Cyanides, such as those of potassium and sodium, are found to be reducing agents (page 634) when fused. Thus, for example, metallic oxides, such as litharge, are converted into the metals, while the concomitant oxidation of the cyanide produces the corresponding cyanate:



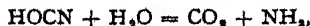
Cyanates are also formed, as already mentioned above, by the action of cyanogen on solutions of potassium or sodium hydroxides.

Potassium cyanate is usually made by heating the cyanide with an oxidizing agent (e.g., litharge, red lead, or potassium permanganate).

The potassium cyanate is extracted by lixiviating the mass with dilute alcohol, and concentrating the alcoholic solution by evaporation. Potassium cyanate is a colourless crystalline powder readily soluble in water and in dilute alcohol. The aqueous solution readily decomposes:

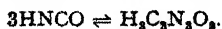


The corresponding acid, HOCN, decomposes so rapidly into carbon dioxide and ammonia:



that cyanic acid cannot be prepared by the decomposition of its salts with mineral acids.

Pure cyanic acid is a colourless gas which condenses in a freezing mixture to an unstable liquid. It is obtained by heating cyanuric acid,  $\text{H}_3\text{C}_3\text{N}_3\text{O}_3$ , which is formed when urea is distilled. On keeping, it soon repolymerizes to cyanuric acid:



Ammonium cyanate is of historical interest and importance, since, on heating, it passes into urea, this being the classical experiment by which in 1829 Wöhler showed that there was no *essential* distinction between inorganic and organic chemistry.

### § 36 Combustion and Flame

The subject of combustion is inextricably interwoven with the history of the elucidation of the nature of the atmosphere, and of the Phlogiston Theory. These matters have been referred to in Chapter 1, and Lavoisier's work, and that of others who led the way for him, will receive some attention in Chapter 26. Meanwhile, some account of the phenomena of combustion itself and of the nature of flame is appropriate at this point.

Combustion, broadly speaking, may be said to be a reaction taking place at a high temperature, and accompanied by the evolution of sufficient heat to maintain the temperature of the reaction. This can be understood by reference to familiar examples.

Thus, carbon in the form of charcoal burns in air. It has to be heated to a temperature of about  $500^\circ$  in order to start the reaction:



As the equation shows, considerable heat is evolved when this reaction takes place, more than sufficient in fact to keep the charcoal at a sufficiently high temperature for the reaction to continue.

But a substance like mercury will not burn in air. If its temperature is raised suitably it will, as in the classical experiments of Lavoisier, combine with the oxygen of the air forming mercuric oxide (page 581); but the amount of heat evolved in this process is insufficient of itself to keep the temperature of the mercury sufficiently high for the reaction to proceed.

Combustion is, further, a process attended by the development of light and heat, e.g., charcoal as before, or a candle. At one time combustion was thought of as being this kind of process, taking place in air or oxygen only. It is not now usual to restrict the term in this way; it is used to cover all self-maintaining reactions attended with the development of light and heat. So that, for example, we speak of the combustion (or burning) of magnesium in carbon dioxide (page 394).

It is customary and convenient to distinguish between the combustible substance and the supporter of combustion. Thus, when a jet of

coal gas burns in air, the gas is said to be combustible, and the air (or the oxygen it contains) is said to be a supporter of combustion. There is a sense, however, in which this distinction is quite arbitrary, depending upon which gas is being supplied at a jet, and which comprises the atmosphere surrounding it.

This can be illustrated by the following experiment:

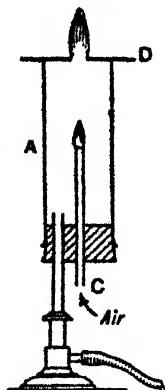


FIG. 22.19.  
Reciprocal  
Combustion

An ordinary lamp cylinder—*A*, Fig. 22.19—may be closed at one end with a cork perforated to fit over a bunsen burner *B*, and also with a hole in which a glass tube *C*—about 10 cm. long and 1 cm. diameter—is fitted. The top of the cylinder is covered with a sheet of asbestos *D*—6 or 7 cm. square—and perforated with a round hole about 2 cm. diameter. The air holes of the bunsen burner are closed; the gas is turned on and the opening in the asbestos is closed by laying a piece of cardboard loosely on the hole. In a few minutes, the apparatus will be filled with coal gas. Light the gas as it issues from *C*, and simultaneously remove the cardboard which was closing the hole in the asbestos. The flame will pass up the tube drawing the air after it. The upward current of gas causes an upward current of air in the tube *C* which burns with a feebly luminous flame in the atmosphere of coal gas. The excess of coal gas issuing from the opening in the asbestos may be ignited, and the two flames show air burning in coal gas, and coal gas burning in air.

### Flame

The development of flame during combustion is quite an accidental feature. Iron burning in oxygen gives no perceptible flame. The intense light is due to the incandescent solid. Similar remarks apply generally to the combustion of solids which are not volatilized at the temperature developed during combustion. On the other hand, phosphorus, sulphur, bitumen, fat, wax, etc., burn with a flame because these solids are volatilized at the temperature of combustion.

The flame of most of the combustible gases has quite a characteristic appearance—sulphur burns in air with a lavender-blue flame; burning hydrogen is scarcely visible in bright daylight, provided the gas and air are free from dust; carbon monoxide has a rich blue flame, silicon hydride a pale green flame, the cyanogen flame has a delicate pink tinge, acetylene burns with a highly luminous yellowish flame, while marsh gas burns with a pale blue, almost non-luminous flame.

It will be obvious that when a stream of gas issues from a tube, the gas can only burn at its surface of contact with the air. The shape of the flame issuing from, say, a circular jet is due to the fact that as the gas issues from the jet, a ring of gas, so to speak, next to the tube

burns first; before any more gas can come in contact with the air and burn, it must rise past the first ring of flame, and each successive layer of gas has to pass higher and higher before it can find the supply of air necessary for combustion. The flame thus assumes the form of a cone.

It would be expected from the foregoing that in the interior of such a cone of flame, where the gas cannot come into contact with the air, and hence cannot react with it, there will be a region of **unburnt gas**. This is easily shown to be the case by experiments such as the following:

(1) Cross-sections of the flame can be shown by depressing thin sheets of asbestos paper (say, 15 cm. square) for a few moments on the flame of, say, a bunsen burner protected from draughts. The hotter portions of the flame where the gases are burning char the paper, producing a dark ring when the paper is held



FIG. 22.20.  
Flame Sections

horizontally, Fig. 22.20, *B*, and a more or less elongated cone if the paper be held vertically in the flame *A*, Fig. 22.20. The particular "flame figure" produced depends on the part of the flame in which the paper is held. (N. Teclu (1891).)

(2) A 5-7 cm. funnel is connected with the gas supply as illustrated in Fig. 22.21. The broad mouth of the funnel is covered with a piece of fine copper or brass wire gauze. A small conical heap of gunpowder ( $1\frac{1}{2}$  cm. base) is placed on the middle of the gauze. The gas is turned on, and a lighted taper slowly depressed from above downwards to the funnel until the gas is ignited. The gunpowder remains on the gauze unconsumed. Ordinary matches can be thrust through the flame and laid on the heap of gunpowder without being ignited.

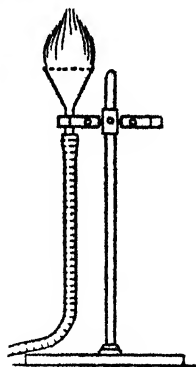
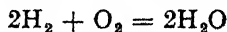


FIG. 22.21.  
Hollow Flame

Flames differ considerably in the details of their "construction" according to the nature of the gas or vapour which is burning. For the present, two types of flame will be considered, the single-mantled flame (typified by hydrogen burning in air) and the double-mantled flame (exemplified by a candle or coal-gas flame).

### Single-mantled Flames

The flame of hydrogen burning in air or oxygen (Fig. 22.22) consists of two cones, an inner one, of unburnt gas, and an outer one, in which (presumably) the single reaction



is taking place. This is the simplest kind of flame.

### Double-mantled Flames

The flames of burning hydrocarbons are much more complex, however, owing to the more complicated series of reactions which are taking place in them.



FIG. 22.22.  
Hydrogen  
Flame

In a candle flame (Fig. 22.23) or a coal-gas flame (that is, the *luminous* gas flame, *not* the so-called bunsen flame, concerning which see below, page 417), four distinct regions may be distinguished. These are:

- (i) the dark, inner zone of unburnt gas or vapour;
- (ii) a yellowish-white brightly luminous region or mantle;
- (iii) a small bright blue region at the base of the flame;
- (iv) a faintly visible outer mantle completely enveloping the rest of the flame.

In the case of the gas flame, when the flame is gradually lowered, the inner luminous sheath gradually diminishes in size, and finally disappears. At the same time, the blue region at the base becomes continuous right across the flame, Fig. 22.24.

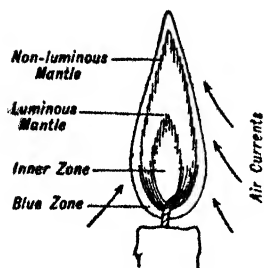


FIG. 22.23.  
Candle Flame

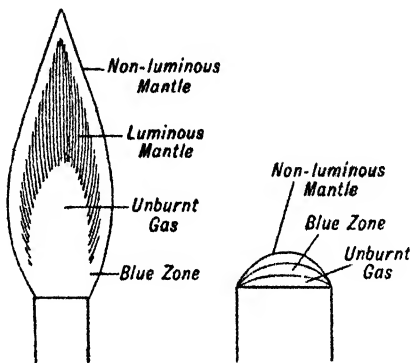


FIG. 22.24.—Flames of Coal Gas

The chemical reactions which occur in the flames of burning hydrocarbons have not been satisfactorily elucidated, although a little is known. Tapping the gases from different parts of the flame by means of platinum or porcelain tubes connected with an aspirator is not very satisfactory because of the changed conditions arising when the reactions take place in contact with solids. Hence, the "proof" that the flame of burning hydrogen sulphide contains free sulphur, and that the luminous mantle of burning hydrocarbons contains free carbon, because a cold dish held in the flame receives a deposit of the respective solids, is quite unsatisfactory. It is conceivable that the hydrogen sulphide flame contains free sulphur, and the hydrocarbon flame free carbon when cold porcelain is held in these flames, but not when this disturbing agent is absent; we therefore prefer demonstrations with methods which do not interfere with the flame itself.

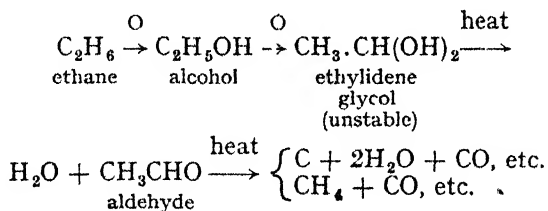
The following is an outline of what is now thought to be the probable nature of the processes which give rise to flames such as have just been described.

In the case of the gas flame, the burning material is gaseous at the start; but in the candle, the heat of the flame causes the hydrocarbons of the wax to melt, rise up the wick and vaporize therefrom. In both flames there is, therefore, a region of comparatively cool unburnt gas or vapour. This is the inner dark zone. At the bottom of this region, some of the gas or vapour meets the uprising air, and complete combustion takes place without the separation of any solid particles. This gives rise to the dark blue zone.

Most of the gas or vapour, however, is decomposed higher up the flame, giving rise to the luminous zone owing to the separation of minute particles of carbon which are raised to a high temperature and hence glow, emitting a yellowish-white light. The separation of particles of carbon in this way was formerly explained by the theory of *preferential combustion*, according to which, in a limited supply of air (such as is the case in the inner mantle of a luminous gas flame), the hydrogen of a hydrocarbon burns first, leaving free carbon. Thus, in the case of ethylene,



That is to say, the hydrogen was believed to burn first in preference to the carbon. Modern experimental work, notably that of Bone and his collaborators, has shown that if there be any such preference it is, in fact, the other way round. They have adduced evidence which suggests that the process takes place by way of hydroxylation, and suggest that the combustion of a hydrocarbon, such as ethane, takes place by way of a series of reactions somewhat as follows:



The process is quite likely more complex, but there is a good deal to suggest that this represents its broad outlines.

In the luminous zone, then, a partial combustion takes place which becomes more or less complete in the outermost, non-luminous mantle. Here the carbon and other products of the incomplete combustion come into contact with a plentiful supply of oxygen from the air. The combustion may not be absolutely complete even here, however, since the air exercises a considerable cooling effect, and occasionally also, even here, the supply of oxygen may not be quite sufficient if the supply of combustible material is very free. In this event the flame smokes.

### § 37 The Luminosity of Flames

It is a well-known fact that many gases give flames which are very bright or luminous. Examples are unsaturated hydrocarbons like ethylene, the vapours of some metals, and phosphorus.

A general explanation of this luminosity is not known. At one period it was believed that all luminous flames contain white-hot particles of solid (**Davy's solid particle theory**). It is now known, however, that while some luminous flames do contain such particles, others do not.

The existence of solid particles in the luminous coal-gas flame, for example, has been satisfactorily demonstrated by Soret's optical test (1875) by which it is shown that if the flame of coal gas or of a candle be placed between a strong light and a screen, the luminous portion of the flame throws a dark shadow on the screen, and if the flame be made to smoke, the shadow of the luminous portion extends into the shadow cast by the smoke.

Also the non-luminous portion of the flame gives no shadow. This result was confirmed by Stokes, who focused the image of the sun on to the flame and examined the scattered light. This was found to be polarized—evidence of the existence of minute solid particles. On the other hand, the flames of carbon disulphide and phosphorus, although luminous, are found in this way to contain no solid particles.

In the course of his experiments H. Davy showed that the luminosity of flames is increased by pressure and diminished by rarefaction. The violet-blue sheath of the hydrogen flame becomes green, then yellow, orange, and red as the pressure is *reduced*; and by *increasing* the pressure, the flame becomes luminous. E. Frankland (1867) found a direct relation between the luminosity of flames and the pressure. Using the flame of hydrogen burning under a pressure of 12 atmospheres, a reduction of the pressure to 3 atmospheres diminished the luminosity 99 per cent. Arguing from the fact that luminous flames are known which contain no solids; that dense gases and vapours give flames more luminous than gases of low density; and that feebly luminous flames become luminous when the surrounding atmosphere is compressed, Frankland inferred that the luminosity of ordinary flames such as coal gas is due to the glow of dense hydrocarbons rather than to the presence of solid particles. This is known as **Frankland's dense hydrocarbon theory**.

Lewes considers that the "dense hydrocarbon" in the flame of coal gas and related gases is acetylene, hence the so-called **acetylene theory of luminosity**. In the particular case of hydrocarbon flames, as interpreted in the preceding section, it does not appear that this hypothesis is a complete explanation. When the pressure of the atmosphere is altered, the dense hydrocarbons themselves give opaque flames containing solid matter. The phenomenon is complicated by changes in the conditions of equilibrium of the products of combustion,



and it is probable that the decomposition of the hydrocarbons in the "innermost parts of the flame" is facilitated by increasing the pressure.

However, it is highly probable that dense vapours, as well as incandescent solids, do produce luminosity. Two distinct effects can be observed in burning hydrogen phosphide: a greenish glow caused by the oxidation of the phosphorus which shows best when the phosphide is largely diluted with carbon dioxide; and a yellowish-white light best seen when phosphorus burns in air or oxygen. This is no doubt due to the glowing of phosphorus pentoxide which, although in the state of *vapour*, can be made to emit a yellowish-white glow when the temperature has attained a certain point. Similar results can be obtained with silicon hydride, but in this case the glow is due to *solid* silica.

Just as a variation of pressure modifies the luminosity of burning gases, so does a variation of temperature. The temperature attained by the combustion of gases in oxygen is greater than in air, owing to the absence of diluting nitrogen. In consequence, combustibles burn far more brilliantly in oxygen than in air. The flame of carbon disulphide in air is nothing like so brilliant as in oxygen; the flame of hydrogen phosphide in air is brilliant, but in oxygen the flame is of dazzling brilliance. Phosphorus burns in chlorine with a far more luminous flame when the chlorine is hot than when cold. Carbon monoxide in oxygen burns with a flame appreciably luminous. Similarly with flames known to contain solid matter. Magnesium and silicon hydride burn far more brightly in oxygen than in air. The reason for this behaviour is far from certain.

### § 38 The Bunsen Burner

The ordinary luminous flame of a burning hydrocarbon is unsatisfactory for heating purposes; and, since the invention of the incandescent gas mantle (page 806) for lighting also. The deposition of soot reduces severely the rate at which heat is transferred to the vessel being heated, as well as involving the loss of much of the potential heat energy of the fuel.

Bunsen in 1855 devised the burner, known by his name, to surmount these objections, and it is now, of course, in universal use.

A certain ratio must exist between the proportion of air and gas in the burner tube in order to get the gas to burn quietly with a blue flame—the so-called **Bunsen flame**. If, when the air-holes are fully open, the gas is gradually turned off, a point is reached when the flame begins to flicker, and finally "strikes back," afterwards burning at the bottom of the tube. As a matter of fact, the mixture of air and gas burning in the bunsen burner is explosive; when the gas is burning quietly, the rate at which the flame travels in the explosive mixture of air and gas is less than the rate at which gas is issuing from the burner; when more air or less gas is introduced, the speed at which the explosive flame can travel is increased; when the rate of the explosive flame and

the speed of the gas issuing from the burner are nearly equal the flame reaches the unstable condition; any further increase in the amount of air or decrease in the amount of gas gives an explosive mixture in which the explosive flame can travel faster than the issuing gas; the flame then "strikes back."



FIG. 22.25.  
Bunsen  
Flame

When burning in its most efficient form, a bunsen flame can be seen to consist of two cones, Fig. 22.25.

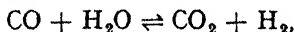
These cones comprise a very pale blue outer mantle, surrounding a bright blue inner cone. Inside the inner cone is a region of unburnt gas. The processes probably taking place in such a flame are as follows. There is a vigorous reaction at the surface of the inner cone, partial oxidation of the gas taking place, and a high temperature being developed. In the outer cone, complete combustion of the carbon monoxide, etc., from the inner cone takes place, but the temperature is not so high.

The processes taking place in the bunsen flame have been investigated by means of Smithell's flame separator.

The apparatus consists of two coaxial tubes, *A* and *B*, Fig. 22.26. The outer wider tube is shorter than the inner tube and fitted with a rubber union, *C*, and a brass clip to permit the outer tube to be slid up and down. The upper ends of the coaxial tubes are fitted one with a mica cylinder *D*, and the other with an aluminium cylinder *E*. The narrower tube is clamped over an unlighted bunsen burner and a loose packing of cotton-wool *F* placed between the burner and the glass tube.

At the beginning of the experiment, the two coaxial tubes are at the same level, the air-holes of the burner are closed, and the gas is lighted at the top of the outer tube, and burns with a luminous flame. The air-holes of the burner are then opened until the flame is non-luminous, and the usual two cones are formed. The outer tube is then slid upwards, and the outer cone ascends with it while the inner cone remains burning at the top of the inner tube.

On analysis, the gas from the space between the two cones was found to consist of nitrogen, carbon monoxide, carbon dioxide, steam, and hydrogen. This mixture was also found to have the same composition if pure methane, unmixed with free hydrogen, was used. This indicates that the reaction taking place in the inner cone leads to the formation of carbon monoxide and hydrogen, and if enough oxygen is present, so that some carbon dioxide is also produced, an equilibrium is set up:



the same as in the production of water gas (page 400).

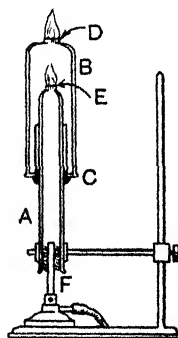


FIG. 22.26  
Smithell's Flame  
Separator

The proportions of gas and air for the normal bunsen flame are approximately 1 part of gas to 2.5 parts of air, and this proportion cannot be greatly exceeded without causing the flame to "strike back." For complete combustion, however, a proportion of about six volumes of air for one of gas is required. Such a mixture clearly cannot be used in a bunsen burner of the ordinary type.

G. Méker, however, has designed a burner in which such a mixture can be burnt—the **Méker burner**. From the sectional diagram, Fig. 22.27, it will be seen that the air-holes are larger than usual, and a deep nickel grid hinders the flame "striking back." Since the gas issuing from the burner has enough air for complete combustion, the flame is practically a "solid cone" of burning gas, and there is no "inner cone of unburnt gas."

The maximum temperature attained in this flame is considerably higher than that of the ordinary bunsen flame.

Another way in which the "theoretical" mixture of gas and air has been employed has been developed by Bone and M'Court. In their heater, the mixture of gas and air (sufficient for complete combustion) passes through a porous diaphragm of refractory material. Gas reactions are, as a rule, catalysed by solid surfaces (page 259) and very rapid combustion therefore takes place in the outer layer of the diaphragm which is raised to a high temperature. No actual flame is visible when the apparatus is working properly, so that it is sometimes referred to as *flameless* or *surface combustion*. Heaters of this kind have been employed for industrial purposes.

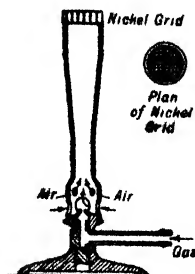


FIG 22.27  
Méker Burner

### § 39 The Safety Lamp

Davy was led to investigate the nature of flames by undertaking an investigation into the causes and prevention of explosions in coal mines. In the course of his experiments, he found that if a flame is cooled

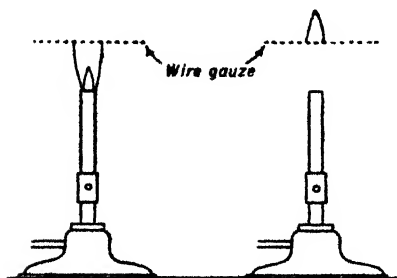


FIG. 22 28 - Effect of Gauze on Flames

sufficiently, it is extinguished, and that different combustible gases have different **ignition points**.

A familiar experiment is the following. A piece of fine wire gauze is held a little above the top of an unlighted bunsen burner. If the gas be turned on and a lighted match is brought above the gauze, the gas is ignited there, but the flame does not pass through the gauze (Fig. 22.28).

Conversely, if the gas be ignited below the gauze, the flame will not pass through, although the passage of inflammable gas through the gauze can be demonstrated by bringing a lighted taper above the gauze. If the gauze be heated red hot, the flame will pass through and burn on both sides.

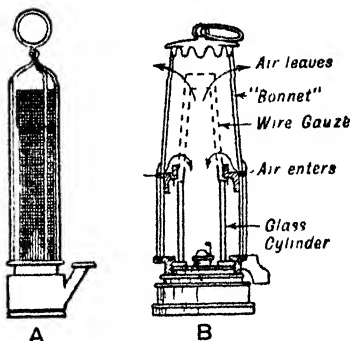


FIG. 22.29  
Safety Lamps (old and new)

Experiments not unlike these led Humphry Davy, in 1815, to produce a "safety lamp for miners." In Davy's original safety lamp, Fig. 22.29, an oil lamp is surrounded by a cylinder made of iron wire gauze, closed at the top with a double layer of gauze, A, Fig. 22.29. When such a lamp is taken into an atmosphere containing a mixture of marsh gas and air, the explosive mixture passes through the gauze and may be ignited inside the cylinder. The flame, however, is unable to pass through the gauze and ignite the mixture outside the cylinder. The modern forms of safety lamp—e.g., *J. B. Marsaul's lamp*, B, Fig. 22.29—allow the lamp to be used under conditions of great danger with a minimum risk of igniting an explosive mixture of firedamp and air. The old Davy safety lamp is obsolete. It gives a very poor illumination owing to the obstruction offered by the wire gauze, and the flame may be forced through the gauze when the current of air exceeds 5 feet per second, and in modern mines the air in some parts of the rapid ventilating roads may attain 20 to 30 feet per second. In the main, however, lighting in coal mines is no longer provided by lamps with flames but with various forms of electric lighting.

## CHAPTER 23

# NITROGEN

What of nitrogen? Is not its apparent great simplicity of action all a sham?  
—M. FARADAY

The fixation of nitrogen is vital to the progress of civilized humanity, and unless we can class it among the certainties to come, the great Caucasian race will cease to be the foremost in the world, and will be squeezed out of existence by the races to whom wheaten bread is not the staff of life.—W. CROOKES.

### § 1 Occurrence and Preparation

It is difficult to state precisely who first isolated nitrogen and recognized it as a definite substance. But D. Rutherford (1772) is generally credited with the discovery of nitrogen. He published a thesis in Latin in 1772 in which he said:

By the respiration of animals, healthy air is not merely rendered mephitic (that is, charged with carbon dioxide), but it also suffers another change, for, after the mephitic portion is absorbed by a solution of caustic alkali, the remaining portion is not rendered salubrious, and, although it occasions no precipitate in lime-water, it nevertheless extinguishes flame, and destroys life

Rutherford removed oxygen from the air by such combustibles as phosphorus, charcoal, etc., and washed out the products of combustion by alkalis or lime-water. The residue was called by him "phlogisticated air."\* H. Cavendish confirmed this experiment in 1785. Lavoisier first called the residue "mephitic air," and afterwards "azote." J. A. C. Chaptal (1823) suggested the name *nitrogène* from the Greek *νίτρον* (*nitron*), saltpetre; and *γεννάω* (*gennao*), I produce—because the gas is a constituent of nitre.

#### Occurrence

Nitrogen constitutes four-fifths of the total volume of atmospheric air. According to spectroscopic observations it is probable that certain nebulae contain nitrogen. It is also found in certain minerals, where it is probably occluded or adsorbed. It occurs combined in ammonia, nitre, and a great many animal and vegetable products—e.g., white of egg, proteids, etc. It is a constant and essential constituent of all living organisms; all life seems to depend upon the transformation of proteid compounds.

#### Preparation

Nitrogen is prepared either:

- (i) from the air by removal of oxygen, etc.;
- (ii) by suitable decomposition of nitrogen compounds.

\* Hydrogen was also called "phlogisticated air."

**From the Air**

Nitrogen is easily obtained from air by removing the admixed carbon dioxide and oxygen. Carbon dioxide is removed by passing the air through a solution of sodium hydroxide; the oxygen is then absorbed by means of an element which will form a non-volatile oxide. Copper turnings are generally considered best for the purpose; the "turnings" offer a large surface of oxidizable metal to the air. The process is as follows:

Air freed from carbon dioxide in a wash-bottle of sodium hydroxide, *A*, Fig. 23.1, and from moisture by passage through sulphuric acid, *B*,

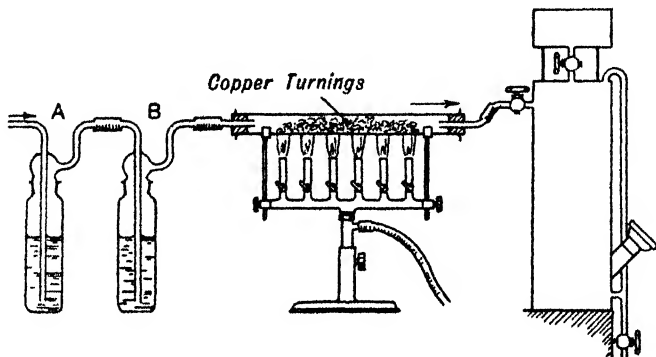
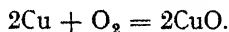


FIG 23 1 —Preparation of Nitrogen

is then passed through a red-hot tube containing copper turnings. The copper removes the oxygen and forms cupric oxide:



The nitrogen passes on to be collected in a gas jar, or gasholder, etc. In the diagram, the air is supposed to be drawn over the copper, the gasholder being filled with nitrogen. If the gasholder were placed at the end *A*, and air forced along the tubes, the nitrogen gas could be collected in gas jars.

Cold boiled water should be used in the gasholder so as to lessen the risk of contamination owing to the presence of oxygen dissolved in ordinary water.

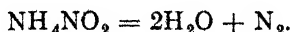
Many attempts have been made to modify this process so as to make it practicable for the production of nitrogen commercially. For example, furnace gases contain large quantities of nitrogen, which can be isolated by passing the gases over a heated mixture of copper and copper oxide to remove any residual oxygen and to oxidize any carbon monoxide. The carbon dioxide is removed by sodium hydroxide, or water under pressure, and nitrogen is left. Nitrogen has also been prepared by burning a mixture of air and hydrogen which is a by-product of many electrolytic processes.

Nitrogen is produced in considerable quantities by the fractionation of liquid air, and is marketed compressed into steel cylinders. This process has been discussed and described in Chapter 3 (page 49). Very large quantities of nitrogen are employed in the synthesis of ammonia by the Haber process (page 429), but for this purpose it is not actually isolated.

In Chapter 26 the discovery that nitrogen extracted from the air, as described above, contains small quantities of other gases, known as the Inert Gases, is described.

### From Nitrogen Compounds

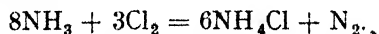
Nitrogen called "chemical nitrogen" can be prepared free from Inert Gases by heating a dilute solution of ammonium nitrite in a glass flask or retort:



The reaction need only be just started by gently warming the flask, it will then continue, and maybe increase in velocity without a further application of heat because the system itself becomes warmer owing to the degradation of energy. If heat be continuously applied to the flask, the reaction may become uncontrollably violent. A mixture of ammonium chloride with a dilute solution of potassium or sodium nitrite may be used instead of ammonium nitrite and is more convenient. Nitrogen is also evolved when ammonium dichromate or a mixture of ammonium chloride and potassium dichromate is heated:



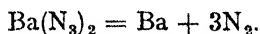
mixtures of hypobromites or hypochlorites with urea also give off nitrogen similarly but these are not suitable for its preparation. The same is true of the action of chlorine on ammonia, since unless the ammonia is in large excess, the dangerous explosive nitrogen trichloride may be formed (page 442):



For the preparation of very pure nitrogen it has been recommended that a mixture of nitric oxide (page 459) and ammonia in the correct proportions be passed over red-hot copper gauze, when the reaction symbolized:



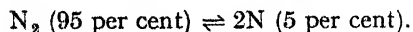
occurs. Very pure nitrogen is also obtained by heating barium azide *in vacuo*:



## § 2 Properties of Nitrogen

Nitrogen is an odourless colourless gas, not quite so dense as air. It is slightly soluble in water; 100 volumes of water at 0° absorb 2.39

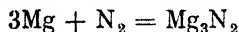
volumes, and at 20°, 1.64 volumes of gas. At 3500° it is estimated that about 5 per cent of the nitrogen is dissociated into atoms:



Nitrogen has been condensed to a colourless liquid which boils at  $-195.8^\circ$  at ordinary atmospheric pressure; and solidifies to a white snow-like mass melting at  $-209.9^\circ$ . Solid nitrogen exists in two forms with a transition temperature  $-237.5^\circ$  and the molecular heat of transformation is 53.8 Cals. Nitrogen cannot be a poisonous gas, for the air we breathe contains a large proportion. The nitrogen dilutes the oxygen as indicated on page 582. Animals die in nitrogen owing to suffocation, i.e., want of oxygen necessary for respiration. Nitrogen is both incombustible and a non-supporter of ordinary combustion.

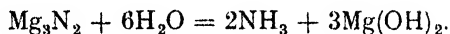
The chief characteristic of nitrogen gas is its chemical inertness, sometimes stated to be owing to "the great affinity of the atoms in the molecule for one another." At any rate, when nitrogen is combined with other elements the converse is true, for the nitrogen compounds generally possess great chemical activity.

The inertness of ordinary nitrogen is a characteristic property at temperatures below 200° C. At and above a dull red heat, however, many metals combine with nitrogen forming derivatives of trivalent nitrogen known as **nitrides**. Magnesium nitride is a typical example:



and is formed in small quantity along with magnesium oxide, when magnesium burns in air.

These nitrides are decomposed by water with the formation of ammonia, e.g.,



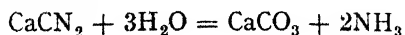
Nitrogen reacts with oxygen to a small extent at very high temperatures forming nitric oxide. This is the basis of the now obsolete Birkeland-Eyde process for the fixation of nitrogen (page 448).

With hydrogen, nitrogen will combine under suitable conditions to form ammonia, a reaction which is utilized in the manufacture of synthetic ammonia by the Haber process (page 429).

Some other non-metallic elements also react to some extent, for example, carbon (which forms cyanogen, page 408), boron and silicon. Nitrogen will also react with calcium carbide at a high temperature forming calcium cyanamide:



which is sold for use as a fertilizer under the name *nitrolim*, since in the soil ammonia is formed





### § 3 Active Nitrogen

In 1910 R. J. Strutt observed that when nitrogen at low pressure is subjected to an electric discharge it shows an "after-glow" when the discharge is stopped. At the same time the chemical properties of the gas are changed, for it becomes reactive, combining directly with sulphur, iodine and phosphorus, and with many metals. It also reacts with acetylene forming hydrocyanic acid and with other organic compounds. On account of this behaviour it has been called **active nitrogen**.

It has been found that a trace of oxygen, mercury vapour or certain other substances is necessary for active nitrogen to be formed, although excess destroys it.

The glow appears to be a surface reaction on the walls of the containing vessel; it depends on the nature of the surface for it does not occur with quartz vessels which have been treated so as to remove all adsorbed oxygen.

The nature of active nitrogen was, for long, uncertain. Strutt suggested that it is atomic nitrogen, but this was doubted, since the energy required, in fact, to produce active nitrogen is said to be less than that required to bring about the dissociation  $N_2 \rightarrow 2N$ .

It has now been shown (Linnett, 1958) that the only species present in active nitrogen in appreciable concentrations are atoms and molecules in the ground state. The former are responsible for the chemical reactivity and, presumably, for the glow also. It has also been shown that charged particles play no part in the production of the glow.

### § 4 Uses of Nitrogen

Nitrogen is used on a very large scale for the manufacture of synthetic ammonia (page 429). Smaller quantities of nitrogen are used for gas-filled electric lamps, and high-temperature thermometers. Nitrogen is also used in order to provide an inert atmosphere in certain industrial processes, e.g., in metallurgy to prevent oxidation or decarburization.

### § 5 Formula and Atomic Weight of Nitrogen

The molecule of nitrogen is believed to be diatomic for the following reasons. Firstly, the ratio of the specific heats (page 84) is 1.4 approximately; and secondly, when ammonia reacts with chlorine or is exploded with oxygen, one volume of nitrogen is formed from two volumes of ammonia (page 435).

The molecular weight of the volatile compounds of nitrogen indicates a value round about 14 for the atomic weight of nitrogen. The exact value has been determined both by chemical and physical methods.

The chief chemical method has been the determination of the proportion of nitrogen in one or other of the oxides. The principle involved is the decomposition of an exactly known weight of the oxide by an electrically heated spiral of iron, or nickel wire. The metal combines with the oxygen and nitrogen remains.

The increase in weight of the metal gives the weight of oxygen in a known weight of oxide. The composition of nitric oxide was determined with a high order of accuracy by this method by Gray in 1905 (see page 463).

Richards's value for the atomic weight of nitrogen is 14.008 (see page 106).

The limiting density method (page 111) has been applied with success to the determination of the atomic weight of nitrogen by Gray, who obtained the value 14.008. Similar work by Moles and his collaborators has led to the same value, which is that at present used as the International Value. A further series of experiments by Cawood and Patterson (1936), using an improved microbalance for the determination of the limiting density of nitrous oxide, gave the value 14.007.

### § 6 Detection and Determination of Nitrogen

By reason of its inertness at ordinary temperatures, nitrogen is usually identified in a negative way, i.e., by its failure to respond to tests for other gases. Thus, a sample of gas which does not support combustion, does not burn, is colourless, neutral and does not react with usual reagents (e.g., lime-water), is probably nitrogen. Confirmation is usually sought by passing the suspected gas over heated calcium or magnesium and treating the product with water. The formation of ammonia indicates the presence of nitrogen in the original gas.

The proportion of nitrogen in a gaseous mixture is similarly determined by removing other gases and measuring the volume of remaining nitrogen and inert gases. The separation of these latter is tedious and difficult (see Chapter 26). The determination of the proportion of nitrogen in the air is described in the same chapter.

The percentage of nitrogen in a compound is often determined by Kjeldahl's process, which depends upon the fact that many compounds yield their nitrogen in the form of ammonium sulphate when heated with concentrated sulphuric acid. The ammonia formed is then liberated and determined, as described on page 437. Nitrogen in nitrates (or in organic compounds containing a nitro-group) which do not form ammonia with sulphuric acid can be determined by means of Devarda's alloy (aluminium, 45 per cent; copper, 50 per cent; and zinc, 5 per cent), which reduces them to ammonia in the presence of alkali.

### § 7 Hydrides of Nitrogen. Ammonia

Nitrogen forms three distinctive compounds with hydrogen, viz.,

Ammonia,  $\text{NH}_3$

Hydrazine,  $\text{N}_2\text{H}_4$

Hydrazoic acid,  $\text{N}_3\text{H}$

of which the first is the most important. The salts of hydrazoic acid with ammonia and hydrazine have the formulae  $\text{N}_4\text{H}_4$  and  $\text{N}_5\text{H}_5$  respectively and are, in one sense, hydrides of nitrogen.

## History and Occurrence of Ammonia

### History

Ammonia was known to the early chemists, and Geber describes the preparation of ammonium chloride by heating urine and common salt. Hence the alchemists' term—*spiritus salis urinae*. Ammonium chloride was first brought to Europe from Egypt, where it was prepared from the "soot" obtained by burning camel's dung.

In 1727 S. Hales noticed that when lime was heated with sal ammoniac in a retort arranged to collect the gas over water, no gas appeared to be given off; on the contrary, water was sucked into the retort; when J. Priestley (1774) tried the experiment with a mercury gas trough, he obtained ammonia gas which he called "alkaline air." C. L. Berthollet (1785), H. Davy (1800), and others established the composition of the gas.

### Occurrence

Small quantities of ammonia occur in atmospheric air and in natural waters. It is produced by the action of putrefying bacteria (page 443) on organic matter in the soil, etc. The odour of ammonia can often be detected near stables. Ammonium salts are also deposited on the sides of craters and fissures of the lava streams of active volcanoes; and with boric acid in the fumaroles of Tuscany.

## § 8 Preparation of Ammonia

Ammonia is usually prepared in the laboratory by the action of alkalis on ammonium salts. It is sometimes convenient to use commercial so-called "liquid" ammonia, from which the gas is driven off on heating, as a source of ammonia in the laboratory, but this is hardly to be dignified by the term "preparation." For laboratory work the use of a cylinder of liquid ammonia is becoming increasingly common. Industrially, large quantities are contained in the ammoniacal liquor of the gasworks and recovery coke oven plant (pages 378–87); it is now manufactured on a very large scale directly from its elements by the Haber process (page 429).

The following reactions, which result in the formation of ammonia, are of some theoretical or historical interest.

Ammonia is formed during the putrefaction of organic compounds, and when nitrogenous compounds such as coal, leather or bones are heated in closed vessels. The old term for ammonia—*spiritus cornus cervi* (spirit of hartshorn)—refers to an old custom of preparing ammonia by heating hoofs and horns of stags in closed vessels. The formation of ammonia by heating nitrogenous compounds in closed vessels is particularly noticeable if the organic matter be heated with soda lime (quicklime slaked with a concentrated solution of sodium hydroxide).

The reduction of nitrates and nitrites by means of nascent hydrogen

(e.g., from Devarda's alloy and alkali) also results in the formation of ammonia. (Cf. page 426.)

### Laboratory Preparation of Ammonia

The familiar laboratory preparation of ammonia is by the action of heat on a mixture of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and slaked lime in a tube as shown in Fig. 23.2. The reaction is represented by the equation:

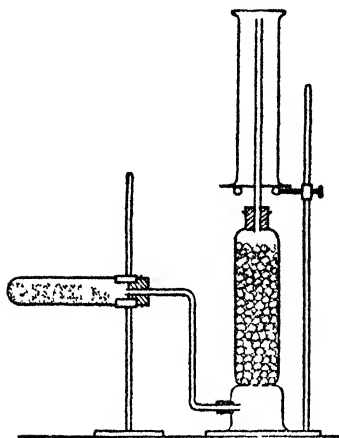
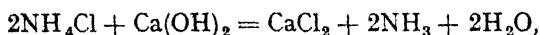


FIG 23 2  
Preparation of Ammonia

so that water is evolved along with the ammonia.

Moist ammonia combines with the ordinary drying agents—calcium chloride, sulphuric acid, phosphorus pentoxide—and accordingly these agents must not be used with the idea of drying the gas. A tower of quick-lime is generally employed.

Ammonia is extremely soluble in water and therefore it is collected by upward delivery, as shown in the diagram. It can be collected over mercury if desired.

A similar apparatus for drying and collection may be employed if it is desired to liberate a sample of the gas from the concentrated commercial solution.

### Industrial Preparation

The manufacture of ammonia falls, as shown, under two headings, viz.,

- (1) recovery as a by-product of coal distillation;
- (2) synthetic production.

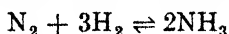
#### *Ammonia from Coal*

It has been pointed out in the preceding chapter (page 378) that in the process of the carbonization of coal, whether in coal-gas manufacture or for coke production, there is produced a considerable quantity of ammonia, which is ultimately absorbed in water, partly as free ammonia, partly as salts such as the carbonate, cyanide, sulphide, etc. This was formerly the source of most of the world's ammonia supply. These ammoniacal liquors are, first of all, heated by means of steam which drives off the free ammonia and also that combined as carbonate. After no more ammonia will come off by this heating, milk of lime is added and the heating continued. The remaining

ammonium salts are thus decomposed and the ammonia driven off. The mixture of free ammonia and steam obtained in both stages of this process is usually absorbed by means of sulphuric acid, so that a solution of ammonium sulphate results, from which crystals of the salt can be obtained.

### *Commercial Synthesis of Ammonia*

The two gases nitrogen and hydrogen do not react under ordinary conditions, but when subjected to the action of electric sparks a mixture in the proportion of three volumes of hydrogen to one of nitrogen reacts to form ammonia to the extent of about 2 per cent. If ammonia gas be similarly sparked, decomposition takes place until only about 2 per cent of ammonia remains. The equilibrium represented



thus lies far over to the left-hand side in these circumstances.

The formation of ammonia from its elements is an exothermic reaction (page 239). In fact,



It is evident, therefore, that according to the principle of Le Chatelier (page 247), since formation of ammonia is attended by reduction in volume and evolution of heat, the equilibrium proportion of ammonia will be greater the higher the pressure and the lower the temperature, which gives broadly the conditions which must be satisfied for a successful synthesis. (See Table XXII, page 249.)

In regard to the use of a low temperature, it is necessary to effect a compromise since the speed of any given reaction is very greatly reduced as the temperature is lowered (page 251). This points to the use of a catalyst so that the speed of the reaction may be reasonably great at a temperature at which the equilibrium proportion of ammonia is sufficiently high to be worth while.

These considerations form the theoretical basis of the Haber process for the manufacture of synthetic ammonia. A mixture of nitrogen and hydrogen, in the proportion of 1 : 3 by volume, is passed over a catalyst at a pressure of about 200 atmospheres and a temperature of 500°.

The mixture required is usually obtained from water gas (pages 289 and 400) and producer gas (page 399) mixed in the correct proportions. Steam is added and the whole passed over heated ferric oxide, which acts as a catalyst converting the monoxide and steam into carbon dioxide and hydrogen (cf. page 289). Carbon dioxide is removed by water under pressure (25 atm.) and residual carbon monoxide by ammoniacal sodium formate (at 250 atm.). The exact nature of the catalyst used for the ammonia synthesis is not quite certain, but, so far as can be judged from the patent literature, its basis is pure iron, to which is added a promoter (page 260). The usual promoter appears to

be about 1 per cent of sodium or potassium oxide and about the same amount of silica or alumina.

Under manufacturing conditions the percentage of ammonia formed is only of the order of 10 per cent, so that it is necessary to remove it without releasing the pressure so that the residual nitrogen and hydrogen can be passed over the catalyst again. The heat of the reaction serves to maintain the necessary temperature once the process has got under way; a heat-interchanger being employed to prevent loss of heat with the issuing gases. The ammonia formed is removed by liquefaction, passage through a spiral tube immersed in cold water being adequate for this purpose at the high pressures employed. Inert Gases (page 588) gradually accumulate in the system and are blown off from time to time.

The general arrangement of the plant may be understood from Fig. 23.3.

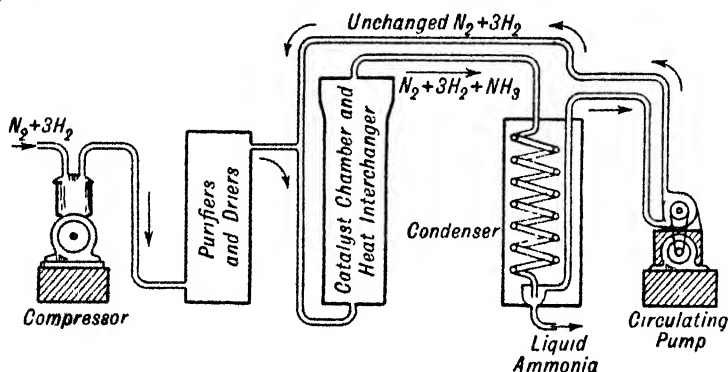
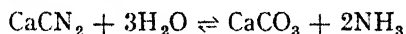


FIG. 23.3 -- The Haber Process (diagrammatic)

Calcium cyanamide (page 424) has also been used as a commercial source of ammonia but its importance is now declining. Powdered cyanamide is stirred with cold water, to decompose any calcium carbide present, and is then treated in an autoclave with steam at 3 atmospheres pressure. Ammonia is formed:



the pressure rises to 12–14 atmospheres and the temperature to 180°. The ammonia is then blown off along with some steam and condensed.

## § 9 Properties of Ammonia

Ammonia is a colourless gas with a pungent odour. If inhaled suddenly, it will bring tears to the eyes; if large quantities be inhaled, suffocation may ensue. Ammonia is a little more than half as dense

as air, and consequently the gas is collected, like hydrogen, by upward delivery.

The gas is extremely soluble in water: one volume of water at 0° and 760 mm. dissolves 1299 volumes of gas, and at 20°, 709 volumes. The gas can all be removed from its aqueous solution by boiling. The great solubility of ammonia in water is illustrated by means of the experiment indicated in Fig. 23.4.

The inverted flask is filled with dry ammonia and then attached to the apparatus as shown. A piece of moistened filter paper *A* is attached to the glass tube just below the jet. This moisture dissolves some of the ammonia, thereby creating a partial vacuum and causing water to be driven up the tube. When this emerges from the jet, the first few drops of water are sufficient to dissolve the whole of the ammonia so that water then rushes out of the jet like a fountain, until the flask is full.

Considerable heat is evolved during the solution of ammonia in water:



If a rapid current of air be driven through a cold solution of ammonia in water, the heat absorbed as the ammonia is expelled from the solution will reduce the temperature sufficiently to freeze a small globule of mercury. The production of cold is best demonstrated by blowing air through a solution of ammonia in a vessel standing on a few drops of water on a block of wood.

The production of cold in this way must not be confused with the use of ammonia in refrigerators and ice-making machines, the operation of which depends upon the properties of liquid ammonia (see below).

Ammonia is readily liquefied, pressure alone being sufficient at ordinary temperatures. The liquid boils at  $-33.4^\circ$  and solidifies to white, transparent crystals at  $-77.7^\circ$ . Like water, liquid ammonia is a bad conductor of heat and electricity, but it is an excellent solvent and many substances which dissolve in it give solutions which conduct electricity (cf. Chapter 15). The behaviour of these solutions has been considerably investigated and there is now an *ammonia chemistry* resembling in many ways the water chemistry with which we are familiar.

### Refrigeration

Liquid ammonia is used in refrigerating machinery, for which purpose it is particularly suitable, since it is very volatile, it is easily obtained

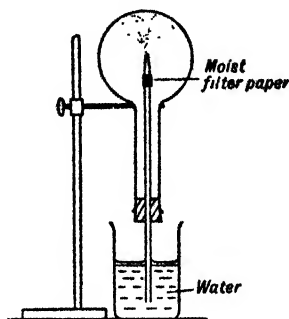
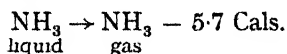


FIG 23.4.  
Ammonia Fountain

and has a high latent heat of vaporization. The heat of evaporation of ammonia is 5.7 Cals. at  $-33^{\circ}\text{C.}$ , i.e.,



If, therefore, liquid ammonia be evaporated, a relatively large amount of heat is absorbed from the surroundings. Fig. 23.5 shows in diagrammatic form the arrangement of a refrigerating plant using ammonia.

Ammonia gas is liquefied by compression in the "condensing coils" by means of a pump; the heat generated as the gas liquefies is conducted away by the cold water flowing over the condensing pipes, Fig. 23.5. The liquid ammonia runs into coils of pipes, "expansion

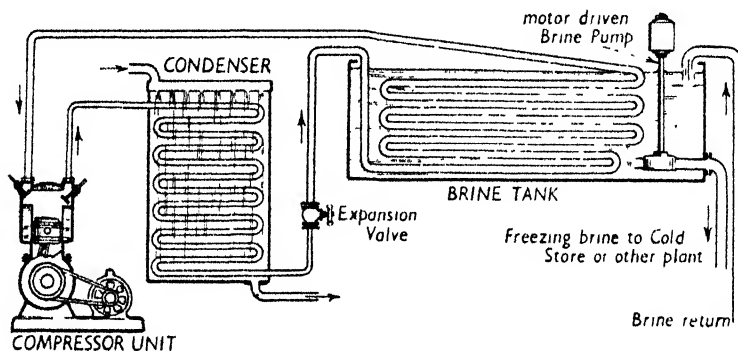


FIG. 23.5. --Refrigerator

coils" dipping in brine. The pressure is removed from the liquid ammonia in the expansion coils, and the heat absorbed by the rapidly evaporating liquid cools the brine\* below zero. The gas from the evaporating liquid is pumped back into the condensing coils; and so the process is continuous. In cold-storage rooms, the cold brine circulates in coils near the ceiling of the room to be cooled, and returns to the cooling tank. Sulphur dioxide, carbon dioxide and particularly fluorochloro derivatives of methane and ethane (freons) are also employed for refrigeration.

Ammonia is a comparatively stable gas at ordinary temperatures; but at a red heat it begins to decompose into nitrogen and hydrogen—a reaction which is merely the reversal of that by which it is formed synthetically (see pages 429-30 above).

Ammonia is a non-supporter of ordinary combustion and does not readily burn in air, but in oxygen it burns with a yellowish flame, while mixtures of ammonia and oxygen are explosive. The combustion of ammonia in oxygen can be demonstrated as indicated in Fig. 23.6.

\* The "brine" used is now usually a solution of calcium chloride.

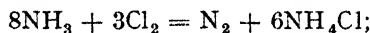


A stream of dry ammonia gas (from a cylinder, for example) is passed through a tube, *A*, which is surrounded by a wider tube, *B*, containing cotton wool and through which a stream of oxygen is passed. If a light be applied to the upper end of *A* the ammonia will burn with a yellowish flame having three cones. The main reaction is represented by the equation:



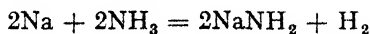
but small quantities of ammonium nitrate and nitrogen peroxide are also formed. In presence of red-hot platinum, ammonia may be oxidized by air or oxygen almost completely to oxides of nitrogen, a reaction which is employed in the manufacture of nitric acid from ammonia (page 448).

Ammonia reacts with chlorine, nitrogen and ammonium chloride being formed if the ammonia is in excess:



but with excess halogen, explosive nitrogen halides result (page 442).

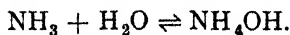
Ammonia reacts with some metals. With the alkali metals amides are formed; for example, sodamide is obtained with sodium and ammonia at a temperature of 300°:



but when magnesium is heated in ammonia gas **magnesium nitride**,  $\text{Mg}_3\text{N}_2$ , is formed.

One of the most striking properties of ammonia, chemically speaking, is the basic character of its aqueous solution. The aqueous solution turns red litmus blue, yellow turmeric paper brown, conducts electricity, and in general reacts like a base.

This behaviour resembles that of aqueous solutions of carbon dioxide (page 393), and just as that solution is believed to contain a certain amount of carbonic acid, resulting from the combination of a proportion of the carbon dioxide with water, so ammonia solutions are believed to contain some **ammonium hydroxide**:



The phase diagram of the system  $\text{NH}_3 - \text{H}_2\text{O}$  has been investigated and indicates the existence of a monohydrate,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . Spectroscopic and thermodynamic data suggest that this monohydrate exists in equilibrium with small amounts of ammonium hydroxide. The ammonium hydroxide appears to be almost completely ionized in which case the fact that ammonia in solution behaves as a weak base is to be

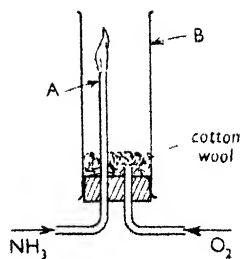


FIG. 23.6.  
Ammonia Burning in  
Oxygen

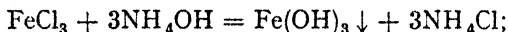
explained by the very low concentration of hydroxide in equilibrium with the hydrate:



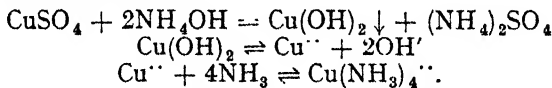
An alternative explanation is that most of the hydroxyl ions are removed from the solution by hydrogen-bonding (page 320) to the nitrogen of the ammonium ion.

If the aqueous solution of ammonia be neutralized with an acid—nitric, sulphuric or hydrochloric acid—the corresponding ammonium salt is formed—ammonium nitrate,  $\text{NH}_4\text{NO}_3$ ; ammonium sulphate,  $\text{NH}_4\text{HSO}_4$ , or  $(\text{NH}_4)_2\text{SO}_4$ ; ammonium chloride,  $\text{NH}_4\text{Cl}$ . It will be observed that we are here dealing with a univalent radical,  $\text{NH}_4$ , which is called **ammonium**. This behaves, in reactions such as those mentioned, in a very similar manner to a sodium atom. The more important ammonium salts are described below.

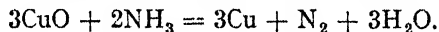
In other ways besides neutralizing acids, a solution of ammonia behaves as a base. Thus, for example, it precipitates many metallic hydroxides from solutions of their salts, and these sometimes dissolve in excess ammonia solution owing to the formation of complex ions. Thus, with ferric salts, ferric hydroxide is precipitated:



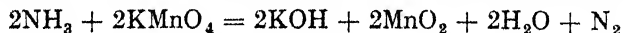
but with copper sulphate solution the cupric hydroxide at first thrown down redissolves in excess of ammonia because of the formation of the complex cuprammonium ion:



Reducing agents are without action on ammonia, but it is fairly easily oxidized, particularly at high temperatures. For example, if a stream of the gas be passed over copper oxide heated in a hard glass tube, the oxide is reduced to copper, and the ammonia oxidized to nitrogen:



(Compare the similar action of hydrogen, page 654.) Oxidizing agents, if sufficiently powerful, will bring about a similar reaction at ordinary temperatures. Thus, for example, with potassium permanganate:



Furthermore, since at high temperatures ammonia dissociates into nitrogen and hydrogen it is under such conditions a powerful reducing agent.

The action of chlorine mentioned on page 433 can be also regarded as an oxidation of ammonia.

The formation from ammonia of complex ions in solution has been mentioned. Many substances containing ammonia combined in this way can be obtained in a crystalline state. This is particularly true

of the compounds containing cobalt and platinum which are known as cobalt-ammines and platinum-ammines respectively. These are discussed on pages 946–51. Ammonia also forms double compounds with substances such as calcium chloride, e.g.,  $\text{CaCl}_2 \cdot 2\text{NH}_3$ ;  $\text{CaCl}_2 \cdot 4\text{NH}_3$ ;  $\text{CaCl}_2 \cdot 8\text{NH}_3$ ; and similar compounds of zinc, aluminium and mercury are known.

### § 10 Uses of Ammonia

Ammonia finds many important applications. Its use for refrigerating purposes has been discussed. In the form of its salts (e.g., the sulphate) it is a valuable and important fertilizer (pages 439–40). It is used also in the manufacture of urea (the other raw material being carbon dioxide) which is an extremely valuable fertilizer, the use of which is increasing. Urea is also used in the manufacture of synthetic resins, particularly of a glass-like kind. Ammonia is employed as a cleansing agent on account of its property of dissolving greases; in the manufacture of sodium carbonate by the Solvay process (q.v.) and in chemical operations where a volatile alkali is needed, etc.

Ammonia is now used industrially as a source of hydrogen for many purposes, e.g., to maintain a reducing atmosphere when galvanizing steel sheets by continuous processes. It is used also in the manufacture of artificial silk by the cuprammonium process (page 655), and in the production of nylon, as "cracked" (i.e., heat-dissociated) ammonia for the production of an atmosphere for the bright annealing of metals, and in the process of *nitriding* (page 915).

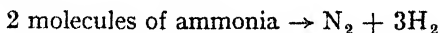
### § 11 Formula of Ammonia

As indicated above (page 429), when ammonia gas is sparked for a long time, about 98 per cent of the gas is decomposed into its elements, and if the experiment be performed in an eudiometer it is found that the volume is almost doubled. If oxygen be now added and the mixture sparked, the hydrogen will be removed as water and the volume of the residual nitrogen is found to be very close to half that of the original ammonia. Neglecting the slight amount of ammonia undecomposed by the sparking, and the slight traces of oxides of nitrogen formed in the explosion with oxygen, it is found that:

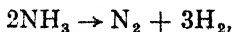
2 volumes of ammonia form 1 volume of nitrogen plus 3 volumes of hydrogen.

Applying Avogadro's hypothesis it follows that:

2 molecules ammonia  $\rightarrow$  1 molecule of nitrogen + 3 molecules of hydrogen. Since the molecules of hydrogen (page 294) and nitrogen (page 425) are known to be diatomic,



whence:



that is to say, the formula of ammonia is  $\text{NH}_3$ . This experiment, and associated reasoning, serves to establish  $\text{NH}_3$  as the *molecular* formula of ammonia and not merely the empirical formula.

The volumetric composition of ammonia may also be demonstrated by the following experiment (sometimes known as Hofmann's experiment). A long tube *A* (Fig. 23.7), marked off into three equal volumes and fitted with a tap as shown, is filled with chlorine. The tube is immersed in water and concentrated ammonia solution is run in from the space above the tap, drop by drop, until the reaction between the chlorine and the ammonia ceases. The first drop of ammonia gives a yellowish-green flame; as more ammonia is added, dense clouds of ammonium chloride are formed and much heat is evolved. When an excess of ammonia has been added, the excess is neutralized with dilute sulphuric acid. The gas in the tube was originally at atmospheric pressure; it is now under reduced pressure. The tube above the tap and a tube *B* are filled with boiled water and attached to *A*; the other end of *B* dips into a beaker of boiled water. On opening the stopcock the liquid will run into the tube *A* until it reaches the second mark on the tube. The tube now contains one volume of nitrogen. The interpretation of Hofmann's experiment is as follows: The hydrogen of the ammonia and the chlorine combine in equal volumes to form hydrogen chloride (cf. page 541). The hydrogen chloride combines with the ammonia to form ammonium chloride. The tube originally contained three volumes of chlorine. This chlorine has taken three volumes of hydrogen to form hydrogen chloride, etc. The latter dissolves in the liquid in the tube, and hence is without influence on the volume of the residual nitrogen. The three volumes of hydrogen were combined in the tube with the one volume of nitrogen which remains in the tube.

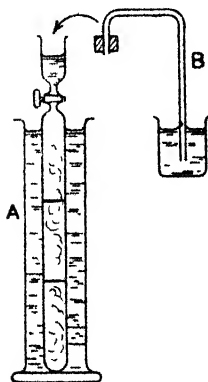


FIG. 23.7  
Hofmann's  
Experiment

The empirical formula of ammonia is therefore  $(\text{NH}_3)_x$ , but as the vapour density is 8.5 its molecular weight is 17. From this it follows that the value of  $x$  is unity and hence that the formula is  $\text{NH}_3$ .

The gravimetric analysis of ammonia is effected by passing a measured volume of the gas over heated copper oxide, followed by passage over red-hot copper turnings to decompose any oxides of nitrogen which have been formed. The resulting water is absorbed in a weighed calcium chloride tube, weighed and the nitrogen passing along is collected in an evacuated globe and weighed. (Cf. page 586.)

The numbers so obtained give the combining proportions of hydrogen and nitrogen in ammonia. The result shows that 14.01 parts of nitrogen are combined with 3.024 parts of hydrogen.

The gravimetric result does not discriminate between  $\text{NH}_3$  and a multiple of this as the molecular formula of ammonia.

### § 12 Detection and Determination of Ammonia

Ammonia is easily detected by its pungent and characteristic smell, and also by its alkaline reaction with litmus, etc., since no other *gas* (except methylamine and ethylamine) behaves in this way. A very delicate test, used for the detection and determination colorimetrically of minute traces of ammonia in drinking water, is the yellow colour which it gives with **Nessler's solution** (page 730).

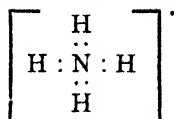
In the ordinary way ammonia is determined by titration, using methyl orange as indicator. The ammonia in an ammonium salt is determined by distilling the salt with excess of sodium hydroxide and passing the distillate into a known volume of standard acid. The excess of acid is determined, after the experiment, by titration with standard alkali in presence of methyl orange.

In the presence of formaldehyde, ammonium salts ("neutralized" to methyl red) form hexamethylene tetramine and the acid which is liberated can be titrated directly with standard alkali. This is another and convenient method for the determination of ammonia in ammonium salts.

### § 13 Ammonium Salts

The basic character of ammonia has been referred to above, and the salts which it forms with acids are known as the ammonium salts, being derived from the hypothetical radical ammonium,  $\text{NH}_4$ . Ammonium salts are white solids, unless they contain a coloured acid radical, and except the perchlorate, cobaltinitrite and chloroplatinate, are readily soluble in water. They decompose or volatilize at temperatures below red heat. When treated with caustic alkalis ammonia is evolved, especially on heating.

The electronic configuration of the ammonium ion will be:



for nitrogen has five electrons in the valency group, and the four hydrogen atoms contribute one each. There would thus be nine electrons available, one more than is required to make the stable group of eight. One is, therefore, lost to the anion, leaving the group with a single positive charge. The ammonium compounds are thus electrovalent substances. The resemblance to the sodium ion, which is a sodium atom which has lost its outermost (valency) electron leaving a completed group of eight, is also apparent.

### Ammonium Chloride, $\text{NH}_4\text{Cl}$

Ammonium chloride is now manufactured from the circulating liquors of the ammonia-soda process (page 620). Clear liquor from the Solvay towers is treated with salt and ammonia until the concentrations of  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and  $\text{CO}_3^{--}$  ions are such that ammonium chloride, and

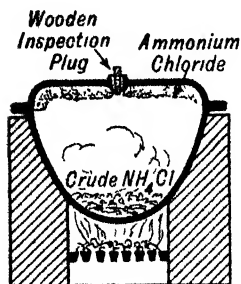


FIG. 23.8.—Sublimation of Ammonium Chloride

not sodium bicarbonate, is deposited on cooling. Very pure ammonium chloride can be obtained, in quantities of 100 tons per day, in this way. Ammonium chloride is a white granular, fibrous, crystalline solid, with a sharp saline taste. It dissolves in water and at the same time lowers the temperature. Ammonium chloride is used for the manufacture of dry batteries, including "dry" cells (page 229), and as a constituent of soldering fluids, to protect metals from oxidation during the soldering. It is also used in galvanizing iron, and in the textile industries.

It is often known as *sal-ammoniac*.

The action of heat on ammonium chloride vapour is interesting. The salt vaporizes at about  $340^\circ\text{C}$ ., and the vapour density at  $350^\circ$  is 14.52 ( $\text{H}_2 = 1$ ), whereas the theoretical value for  $\text{NH}_4\text{Cl}$  is 26.75. That is, the observed density is very little more than half the value which would be predicted. This is explained by supposing that the molecule is dissociated into ammonia and hydrogen chloride:



If complete dissociation occurred, the vapour density would be 13.375 so that it appears that at  $350^\circ$  the vapour contains about 17 per cent of ammonium chloride, and 83 per cent of a mixture of equal volumes of ammonia and hydrogen chloride.

On cooling, the two gases recombine forming ammonium chloride once more, but it is possible to effect a partial separation of the two gases from the hot vapour by diffusion (page 31), thus proving their presence. This can be done by means of the apparatus shown in Fig. 23.9.

A little pure ammonium chloride is placed near the middle of a hard glass tube inclined as shown; a little lower down is a piece of blue litmus paper. A loose plug of asbestos is put above the salt and then a piece of red litmus paper. On heating the ammonium chloride, ammonia being the less dense gas diffuses more quickly than the hydrogen chloride. Consequently, the blue litmus is reddened by the

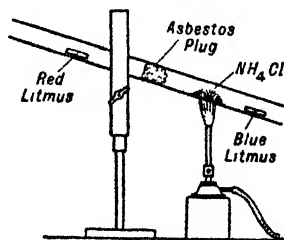


FIG. 23.9 — Dissociation of Ammonium Chloride

excess of slow diffusing hydrogen chloride in the lower part of the tube; and the red litmus is turned blue by the ammonia which passes to the upper part of the tube before the hydrogen chloride.

Notice that this experiment only proves that *some* dissociation takes place; it does not prove complete dissociation as the equilibrium:

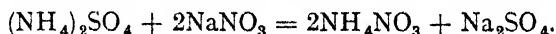


is being disturbed.

Intensively dried ammonia and hydrochloric acid do not combine when mixed, and it has also been claimed by Baker that intensively dried ammonium chloride does not dissociate when heated. There has been much controversy about this point (see page 318) and it is now thought that even intensively dried ammonium chloride does, in fact, undergo some dissociation and that Baker's conclusion was the result of an inaccurate method for measuring the density of the vapour.

### Ammonium Nitrate, $\text{NH}_4\text{NO}_3$

Ammonium nitrate is made by neutralizing concentrated nitric acid with ammonia gas, when the ammonium nitrate remains fused, or by double decomposition of ammonium sulphate and sodium nitrate:



The sodium sulphate crystallizes out with ten molecules of water of crystallization and the ammonium nitrate is recovered by evaporation. It has also been made by the double decomposition of ammonium sulphate and calcium nitrate; by using sodium nitrate instead of sodium chloride in the ammonia-soda process (page 620), and also by partial oxidation of ammonia (page 448).

It exists in colourless crystals which are found in five different forms. It readily dissolves in water, with the absorption of much heat, and so has been employed as a freezing salt, a low temperature being reached when a large amount of the salt is dissolved in a little water. It is also used in the preparation of nitrous oxide (page 457) and of explosives. The explosives *amatol* and *ammonab* consist largely of ammonium nitrate. (*Amatol*, 80 per cent ammonium nitrate and 20 per cent trinitrotoluene; *ammonal*, principally ammonium nitrate, with small quantities of aluminium and sometimes charcoal.) Ammonium nitrate is also used as a fertilizer, for which purpose it is usually mixed with other substances such as ammonium sulphate (*leuna saltpetre*) or calcium carbonate (*nitrochalk*).

### Ammonium Sulphate $(\text{NH}_4)_2\text{SO}_4$

This is the most important commercial salt of ammonia. It is made by passing ammonia gas into 60 per cent sulphuric acid, the salt being obtained by evaporation. It is also made from synthetic ammonia by passing the gas into a suspension of gypsum or anhydrite (calcium sulphate) in water through which a stream of carbon dioxide

is also passing. Calcium carbonate is precipitated and ammonium sulphate remains in solution:



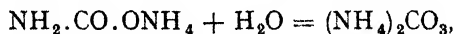
Ammonium sulphate forms large transparent crystals, isomorphous with potassium sulphate. It is very soluble in water. On heating, it loses ammonia even below  $100^\circ$  and forms an **acid sulphate**  $\text{NH}_4 \cdot \text{HSO}_4$ .

Ammonium sulphate is used extensively as a fertilizer and as a source of ammonium compounds.

### Ammonium Carbonate

What is known as ammonium carbonate is made commercially by subliming a mixture of chalk and ammonium chloride or sulphate from iron retorts into lead receivers. There is thus produced a substance which, after resublimation with a little water, comes into the market as a white, semi-transparent fibrous mass covered on the outside with a white opaque powder. This powder is **ammonium bicarbonate**,  $\text{NH}_4 \cdot \text{HCO}_3$ , and the main constituent of the rest of the material is now known to be **ammonium carbamate**,  $\text{NH}_2 \cdot \text{CO} \cdot \text{ONH}_4$ .

Ammonium carbamate reacts with water giving the carbonate:



so that solutions of the solid commercial product contain ammonium carbonate.

### Ammonium Sulphides

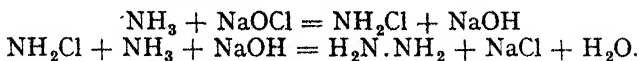
Bineau in 1839 observed the formation of colourless needles when ammonia and hydrogen sulphide are mixed in equal volumes. These are probably composed of **ammonium hydrosulphide** ( $\text{NH}_4 \cdot \text{HS}$ ). If hydrogen sulphide be passed through fairly concentrated ammonia solution the resulting liquid contains a mixture of this hydrosulphide with the normal **ammonium sulphide**— $(\text{NH}_4)_2\text{S}$ . This latter can be obtained by saturating concentrated ammonia solution with hydrogen sulphide, keeping the solution cold. By adding flowers of sulphur (10 parts) to such a solution (200 parts) mixed with concentrated ammonia (200 parts) and shaking until all the sulphur has dissolved *yellow ammonium sulphide*, a solution of various ammonium polysulphides  $(\text{NH}_4)_2\text{S}_n$ , results. The principal constituent is probably the pentasulphide  $(\text{NH}_4)_2\text{S}_5$  (cf. page 479). Solutions of ammonium sulphide (both "colourless" and "yellow") are used in qualitative analysis.

## § 14 Hydrazine

Hydrazine,  $\text{N}_2\text{H}_4$ , is best made by the method discovered by Rashig (1907) by the action of sodium hypochlorite solution on ammonia in the presence of a little glue or gelatine. The reaction takes place in two

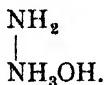


stages: in the first monochloroamine ( $\text{NH}_2\text{Cl}$ ) is formed and this then reacts with a further quantity of ammonia:



The function of the gelatine (or glue) in this preparation is not understood, but if it is not present, no hydrazine is formed. The reaction product is acidified with sulphuric acid and the salt, hydrazine sulphate,  $\text{N}_2\text{H}_5 \cdot \text{HSO}_4$  can then be crystallized out.

Hydrazine is a mono-acid base forming salts such as the sulphate (above) or hydrochloride,  $\text{N}_2\text{H}_5\text{Cl}$ . It is a very weak base, weaker than ammonia. Solutions of caustic alkalis do not liberate hydrazine itself from its salts but form a very stable monohydrate which is often formulated  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  but which may be the true base



Pure anhydrous hydrazine has been obtained by the action of sodium methylate on hydrazine hydrochloride in anhydrous methyl alcohol:

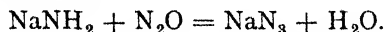


Hydrazine is a colourless liquid which boils at  $113.5^\circ$  at atmospheric pressure and, on cooling, forms a solid which melts at  $1.4^\circ$ . Hydrazine and its salts are powerful reducing agents. Copper, silver, gold and platinum are precipitated from solutions of their salts, ferric salts are reduced to ferrous salts and iodates to iodides. In these reactions the hydrazine is converted into nitrogen and water.

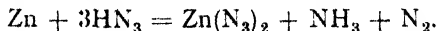
Hydrazine has come into prominence in recent years through its use, in conjunction with hydrogen peroxide, as a fuel in flying bombs and high-speed "rockets."

### § 15 Hydrazoic Acid, $\text{HN}_3$

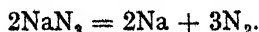
Hydrazoic acid is obtained by distilling its sodium salt (sodium azide,  $\text{NaN}_3$ ) with 50 per cent sulphuric acid. The aqueous distillate is fractionated and the anhydrous acid obtained by distillation over fused calcium chloride. **Sodium azide** is made by passing nitrous oxide over heated sodamide (page 633)



Hydrazoic acid is a colourless mobile liquid with a very unpleasant smell; it melts at  $-80^\circ$  and boils at  $37^\circ$ . It is very poisonous and dangerously explosive. It is a weak acid of about the same strength as acetic acid; its salts are known as azides and it reacts readily with many metals evolving *nitrogen* (not hydrogen) but forming the azide of the metal, e.g.,



The alkali metal azides and barium azide decompose smoothly on heating and so form a source of very pure nitrogen:



The azides of the heavy metals are explosive; lead azide, for example, is used as a detonator being, for some purposes, more efficient than mercury fulminate (page 725).

The vapour density of the acid corresponds with the formula  $\text{HN}_3$ ; examination of crystals of potassium azide by X-rays indicates that the azide ion is linear. It is probable that the structure of the acid should be written  $\text{HN}=\text{N}\rightleftharpoons\text{N}$  (or "electronically"  $\text{H}:\ddot{\text{N}}::\ddot{\text{N}}::\ddot{\text{N}}:$ ). The ion is thought to be a resonance hybrid of the three forms

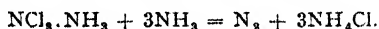


## § 16 The Action of Halogens on Ammonia and Ammonium Salts

Chlorine, bromine and iodine all react with ammonia, and although the final products are very different it is probable that the initial stages are similar.

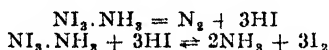
The action of chlorine or bromine upon excess of aqueous ammonia solution results in the liberation of nitrogen and the formation of an ammonium salt. It is probable, however, that in the first place substitution takes place, the resulting trihalogen compound combining with another molecule of ammonia, e.g.,  $\text{NCl}_3.\text{NH}_3$ .

The trichloro and tribromo compounds are very unstable and decompose in presence of excess of ammonia, forming an ammonium salt and free nitrogen:

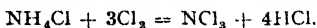


The iodine compound is more stable and separates as the insoluble brownish-black so-called nitrogen iodide (see below). When exposed to light in presence of ammonia, however, this decomposes in the same way as the chlorine and bromine derivatives.

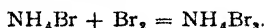
If there be not excess of ammonia present, however, iodine is liberated:



With ammonium salts, the action is different. Chlorine replaces hydrogen in ammonium chloride and yellow oily drops of nitrogen chloride (see below) separate.



Bromine and iodine are unable to replace hydrogen in the ammonium salt, but combine with it forming perhalides, e.g.,



A number of similarly constituted ammonium perhalides is known, one of the most interesting being the tetrachloroiodide  $\text{NH}_4\text{ICl}_4$  which is remarkably stable and was one of the earliest compounds of iodine to be discovered (Fulhol, 1839).

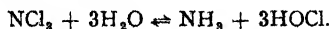
## § 17 Nitrogen Trichloride, $\text{NCl}_3$

Nitrogen chloride was discovered by Dulong in 1811. It separates in yellow drops when chlorine is passed into a solution of ammonium chloride or when such a solution is electrolysed. It is also formed when a lump of ammonium chloride is suspended in a concentrated solution of hypochlorous acid.

Nitrogen chloride is a yellow liquid and dangerously explosive. Its solution in carbon tetrachloride is safer to handle. When such a solution is shaken with excess of concentrated hydrochloric acid, chlorine is liberated:



It is slowly hydrolysed by water into ammonium hypochlorite, this being apparently a reversible reaction (cf. preparation above in which the ammonia is furnished by the ammonium chloride).

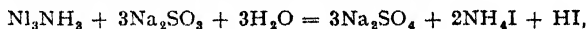


Nitrogen trichloride was formerly used (largely diluted with air) for the bleaching of flour (Agene process). Its use for this purpose is now prohibited and chlorine dioxide (page 544) is used instead.

### § 18 Nitrogen Iodide, $\text{NI}_3 \cdot \text{NH}_3$

The brownish-black solid which separates when iodine is added to excess of aqueous ammonia is known as nitrogen iodide and was formerly thought to vary in composition according to the mode of preparation. Chattaway has, however, definitely established the fact that a single definite compound is always formed, viz.,  $\text{NH}_3 \cdot \text{NI}_3$ , and that the various formulae previously suggested were due to the specimens analysed having partially decomposed, e.g., through exposure to light (cf. § 14). Chattaway showed that this compound could be obtained crystalline with proper precautions.

Nitrogen iodide explodes very readily indeed when dry, but can be handled safely when moistened with ammonia. It reacts with reducing agents with the formation of hydriodic acid, e.g., with sodium sulphite:



a reaction which can be used for its determination, by titrating the free acid with baryta, the iodide with silver nitrate, and the ammonia set free and titrated with acid. The composition was determined in this way.

### § 19 Fixation of Nitrogen. The Nitrogen Cycle

All living matter and the waste products of animals contain considerable quantities of combined nitrogen. It is a necessary constituent for the growth of living organisms. During the decay of organic matter through the agency of bacteria, part of the nitrogen finds its way back to the atmosphere, and part passes directly into the soil to be absorbed by plants. Animals cannot assimilate free nitrogen, and they are accordingly dependent upon the plants for their supply. Plants in light transform inorganic compounds into complex organic products surcharged with energy and which are necessary for the life of higher animals. Plants thus form a permanent link between the inorganic and the animal kingdoms. Plants cannot usually obtain their nitrogen direct from the atmosphere. Most plants get their nitrogen from the soil where it is present in the form of nitrates, ammonium salts, or other complex compounds. The organic matter in the soil is attacked by bacteria of various kinds, and part is converted into nitrates and part into free nitrogen. A certain amount is brought back from the atmosphere during a rain storm, where it has been oxidized into ammonium nitrate by electric discharges—this more

particularly in the polar regions. These supplies of available nitrogen, however, do not suffice to maintain the fertility of cultivated soils. It is therefore necessary to make good the constant draining of the available nitrogen by the cultivated plants. This is done by allowing nitrogenous organic matter—manures—to decay away in the soil, or to add a mixture—a fertilizer—containing available nitrogen.

The considerations outlined in the preceding paragraph indicate the need for supplying nitrogen to the soil to make up for that removed by cultivation. The development of agriculture is largely dependent, therefore, upon the supply of cheap combined nitrogen. The chief sources of supply of combined nitrogen are:

- (i) coal, via the gasworks, page 385;
- (ii) Chile nitrate deposits, page 627;
- (iii) nitre plantations (page 641) and animal excrements;
- (iv) fixation of atmospheric nitrogen.

The last of these is of increasing importance since the atmosphere contains a virtually inexhaustible supply of nitrogen. This matter may be discussed under two heads:

- (i) fixation by bacteria associated with plants;
- (ii) artificial fixation.

In 1853 G. Ville noticed that while most plants reduce the available nitrogen in soils, some plants, principally the leguminosae—peas, beans,

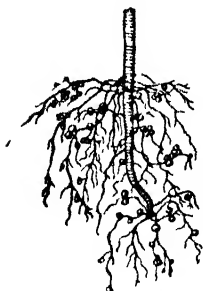


FIG. 23.10. - Nodules on Root of Bean Plant

clover, lupins, etc.—enrich the soil so that more available nitrogen is present after a crop has been removed than before. In 1886 H. Hell showed that certain leguminosae appear to live in a kind of partnership—symbiosis (from the Greek *συν* (*syn*), with; *βίωσις* (*biosis*), living)—with certain bacteria—e.g., the *bacterium radicle*. The bacteria appear to live as guests in nodules on the rootlets of their host, and probably also in the neighbouring soil. The nodules on the rootlets of a *Phaseolus* (bean) are illustrated in Fig. 23.10. The symbiotic bacteria convert the nitrogen of the atmosphere into a form available as food for the plant on which they live.

Of artificial methods for the fixation of atmospheric nitrogen, there are at present available two good ones, viz.,

- (i) the manufacture of calcium cyanamide (page 696);
- (ii) the synthesis of ammonia (page 429) (Haber process).

A third method, the synthesis of nitric oxide (and hence of nitric acid and nitrates)—(page 447) (Birkeland-Eyde process)—was formerly used, but it is now obsolete.

These processes are described on the pages named. The first is particularly suitable for localities where electric power is very cheap, and hence is to be found in operation at Niagara Falls. The second, the Haber process, requires comparatively little power for its operation and so is worked to an increasing extent in England and Germany.

The artificial fixation of nitrogen, a "problem" at the beginning of the present century, is now a common industrial operation.

It is usual to refer to the succession of changes through which nitrogen passes as described in the preceding pages as the **nitrogen cycle** and the processes involved are summarized in some such diagram as Fig. 23.11.

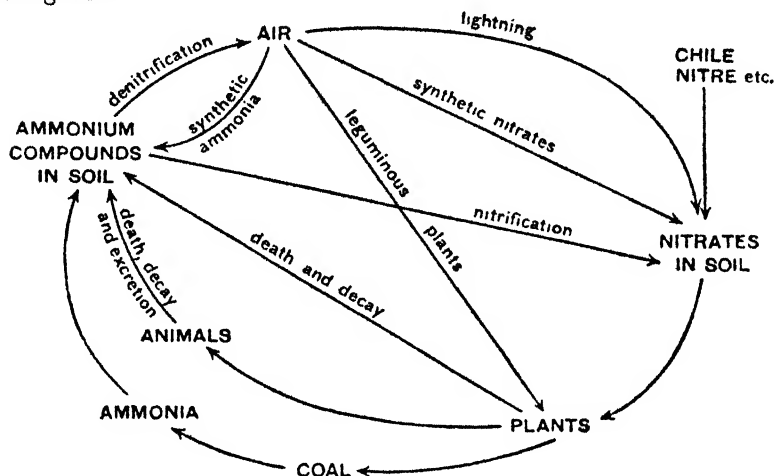


FIG. 23.11 —Nitrogen Cycle

## § 20 Nitric Acid, $\text{HNO}_3$ . History and Occurrence

### History

Nitric acid was probably not known to the ancient Egyptians. Geber says that he made it by distilling copperas (ferrous sulphate) with saltpetre and alum; and J. R. Glauber (1650) made it by distilling a mixture of nitre and sulphuric acid. A. L. Lavoisier (1776) proved that nitric acid is a compound of oxygen, and H. Cavendish (1784-5) demonstrated that it is formed by sparking nitrogen with moist oxygen.

### Occurrence

A little nitric acid is formed in the atmosphere by lightning, causing combination of the oxygen and nitrogen of the air (see page 447 below).

## § 21 Preparation of Nitric Acid

### Laboratory Preparation

Nitric acid is prepared in the laboratory by the action of hot concentrated sulphuric acid on a nitrate, potassium nitrate being usually employed. The experiment is carried out in an apparatus such as that indicated in Fig. 23.12.

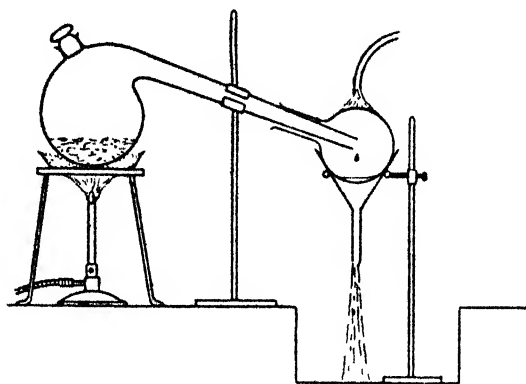
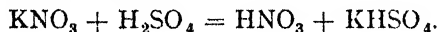


FIG. 23 12 — Preparation of Nitric Acid

The retort is charged with approximately equal weights of sulphuric acid and potassium nitrate, and heated. Brownish-red fumes appear which condense in the cooled receiver to a brown liquid. This liquid is nitric acid, coloured by the presence of a little nitrogen peroxide (page 464), formed by the decomposition of the acid. It is purified by redistillation and by blowing a current of dry air, or carbon dioxide, through the warm nitric acid. The reaction involved in the preparation is represented by the equation:



At the temperature at which the operation can be carried out in glass vessels, potassium bisulphate is formed. At the higher temperatures possible commercially, the normal sulphate results so that less sulphuric acid is required (see below).

The acid so obtained will contain water, a constant boiling mixture (page 449) being formed. If it be redistilled with an equal volume of concentrated sulphuric acid, and a current of dry air or carbon dioxide passed through the warm acid as before, almost pure anhydrous nitric acid is obtained. Crystals of pure nitric acid can be obtained by cooling this acid in a freezing mixture. The **fuming nitric acid** of commerce is made similarly, but usually without having the nitrogen peroxide removed, so that it is brown in colour.

### Industrial Preparation

Nitric acid is now manufactured in two ways, viz.:

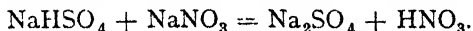
- (i) from sulphuric acid and sodium nitrate (Chile saltpetre);
- (ii) by the oxidation of ammonia.

It was also made for a time by the combination of the nitrogen and oxygen of the air.

Sodium nitrate, also known as Chile saltpetre, is obtained in enormous quantities from the nitre beds of Chile and Peru (page 627), and is used as a source of nitric acid on a large scale.

The sodium nitrate and sulphuric acid are heated in cast-iron retorts; the vapour is condensed in earthenware pipes cooled by water, and collected in earthenware jars. The last jar is connected with a tower filled with coke down which a stream of water trickles. The object is to recover the nitrogen peroxide produced by the decomposition of the nitric acid. The retort has an exit pipe from which the sodium sulphate can be run when the action is over. To reduce the amount of nitrogen peroxide formed during the decomposition of the nitric acid by heat, the stills are often worked under a reduced pressure so that the acid may come off at as low a temperature as possible.

If the temperature be high enough, the reaction indicated in the laboratory preparation is succeeded by that represented:



In some works this is carried out, but the practice is now becoming commoner of stopping the process at the first stage, and utilizing the sodium hydrogen sulphate (known as *nitre-cake*) for the manufacture of sodium sulphate and hydrochloric acid (page 629).

### Manufacture of Nitric Acid from the Air

J. Priestley (1775) first noticed that an acid is formed when moist air is sparked continuously for some time, but he seems to have thought that the acidity was due to carbonic acid. H. Cavendish (1785) proved that the product of the action is nitric acid, while M. Berthelot showed that nitric oxide, NO, is an intermediate stage in the process.

When a mixture of nitrogen and oxygen is raised to a very high temperature, the following equilibrium is set up:



Examination of this equation in the light of Le Chatelier's principle (page 247) shows that the amount of nitric oxide present at equilibrium will be greater at high temperatures, since heat is absorbed in the formation of nitric oxide. Similarly, since there is no volume change in the reaction, changes of pressure will be without influence upon the equilibrium. Investigation of this equilibrium by Nernst has shown that it is only at temperatures above 2000° that a useful yield of nitric oxide is obtainable, and even at 3000° the equilibrium proportion is

only about 5 per cent. The usual means of obtaining such a temperature is by the use of the electric arc, and the commercial application of this reaction known as the Birkeland-Eyde process, which was formerly worked on a large scale in Norway but has now been superseded by the Haber process, utilized a large alternating current arc struck between water-cooled copper poles, and spread out by means of an intense magnetic field into a disc of "flame" about six feet in diameter, through which a stream of air was blown.

As has been said, the proportion of nitric oxide at  $3000^{\circ}$  is about 5 per cent, but at temperatures even as high as  $1500^{\circ}$  this proportion is less than half of 1 per cent, so that it is necessary to cool the gases very quickly so as to "freeze" the equilibrium (see page 251). The rapid passage of the gases and the thinness of the flame made it possible to arrange that the temperature of the exit gases was about  $1000^{\circ}$  and so secure this result. The percentage of nitric oxide actually obtained was round about 1 per cent.

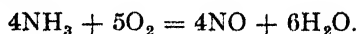
The nitric oxide formed was converted into nitric acid in the way described below for the utilization of the gas formed by the catalytic oxidation of ammonia.

### Manufacture of Nitric Acid from Ammonia

The fact that, in presence of a suitable catalyst, ammonia can be oxidized by the oxygen of the air to nitric oxide, has been mentioned previously (page 433). This has, of late years, been made the basis for the manufacture of nitric acid (indirectly) from the air in countries where synthetic ammonia is being produced in quantity.

A mixture of ammonia and air containing about 10 per cent of ammonia is passed rapidly through a layer of platinum gauze heated to about  $700^{\circ}$  in an apparatus arranged as shown diagrammatically in Fig. 23.13.

The platinum gauze is heated electrically in order to start the reaction; but, once the rate of flow of the gases is properly adjusted, the heat of the reaction itself maintains the necessary temperature.



The exit gases are passed to boilers, where steam is raised and

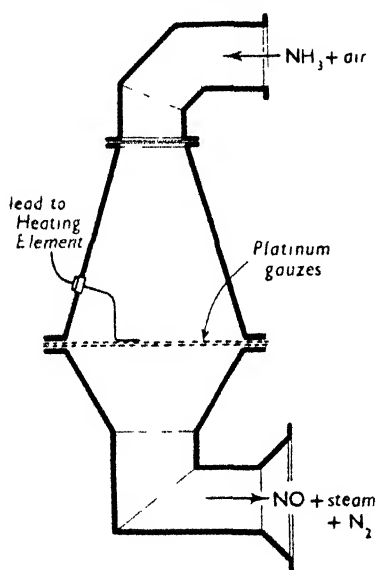
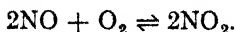


FIG. 23.13.—Ammonia Oxidation (Diagrammatic)



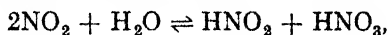
utilized for evaporation and general purposes of the plant, and are finally cooled to about  $50^{\circ}$  in a cooler-condenser.

When the gases have cooled to  $600^{\circ}$  formation of nitrogen peroxide begins:

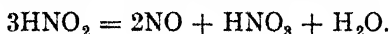


This is a rather slow reaction, and in order that it shall be complete, the gases pass through a large empty iron tower before going to the absorption towers. These absorption towers are built of granite and may be up to eighty feet in height; they are packed with broken quartz over which water is circulating.

The principal reaction taking place in the absorption towers is:



that is, a mixture of nitrous and nitric acids is formed. The nitrous acid, however, decomposes in concentrated solution into nitric acid and nitric oxide:



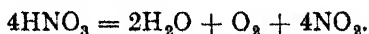
The nitric oxide is reoxidized by the air present and is absorbed again as above. The final gases are absorbed in towers fed with sodium carbonate where sodium nitrite (an important salt, page 628) is formed. From the previous towers, nitric acid of about 30 per cent strength is obtained and is usually neutralized with limestone, thereby forming calcium nitrate, which is sold as a fertilizer under the name of Norwegian saltpetre. Some of the nitric acid, however, is distilled and concentrated and sold as such.

In many modern plants, the whole process is carried out at a pressure of 7-8 atmospheres and the absorption takes place in a water-cooled tower made of chromium steel and containing carefully designed baffles. The heat evolved during absorption can be dissipated more readily than in the old system on account of the conductivity of the steel; consequently a much smaller tower will serve.

## § 22 Properties of Nitric Acid

Nitric acid is a colourless mobile liquid which fumes strongly in air. It has a peculiar smell. The pure acid is hygroscopic and rapidly absorbs moisture from the air. It mixes in all proportions with water; and, as in the case of sulphuric acid, nitric acid contracts when mixed with water, and the mixture rises in temperature. The pure acid boils at  $86^{\circ}$ , and freezes to a white solid, melting at  $-41.3^{\circ}$ . An aqueous solution containing 68 per cent of nitric acid boils at  $120.5^{\circ}$ ; more concentrated solutions, and also more dilute solutions, boil at lower temperatures. A more dilute solution loses water on boiling, and a more concentrated solution loses acid on boiling until 68 per cent of nitric acid of constant boiling point distils unchanged. This is the concentrated nitric acid of commerce. The specific gravity of the constant boiling acid at  $15^{\circ}$  is 1.414, that of the pure acid 1.53 at the same temperature.

Nitric acid is readily decomposed by heat; some decomposition takes place, therefore, during distillation:



It commences below  $68^\circ$  and at higher temperatures is very marked.

The principal chemical properties of nitric acid fall into three main groups, viz., its reactions as

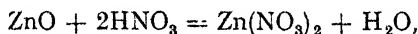
- (i) an acid,
- (ii) an oxidizing agent,
- (iii) a nitrating agent,

though there are, of course, reactions in which it acts in more than one way—for example, its action on copper (page 650).

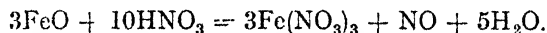
### Nitric Acid as an Acid

Nitric acid is a very strong acid in the sense in which the strength of acids is discussed in Chapter 18 (page 266), where it is shown that, on the basis of the Ionic Theory, nitric and hydrochloric acids are the two strongest acids known.

Nitric acid exhibits the usual general properties of acids in all reactions where its oxidizing properties are not operative. Thus, it reacts in the normal way with basic oxides, hydroxides and carbonates, forming the corresponding salts, unless the metallic radical concerned is a reducing agent. Thus, for example, with zinc oxide the nitrate is formed:



while with ferrous oxide, oxidation also takes place so that the *ferric* salt results:

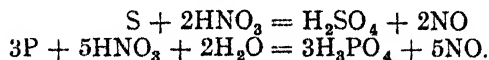


The action of nitric acid on metals (see below) is complicated by the oxidizing actions which take place, the acid acting both as an acid and an oxidizing agent.

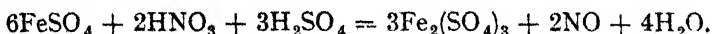
Owing to its volatility, nitric acid is readily turned out of its salts by weaker but less volatile acids. The laboratory preparation, using sulphuric acid, is an example of this.

### Nitric Acid as an Oxidizing Agent

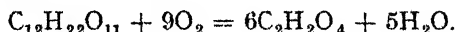
In consequence of the large proportion of oxygen in nitric acid, and of the ease with which it is decomposed, it would be expected that it would be a powerful oxidizing agent. It is so. Thus, for example, sulphur is oxidized to sulphuric acid, and phosphorus to phosphoric acid:



Ferrous sulphate is similarly oxidized to ferric sulphate in the presence of sulphuric acid:



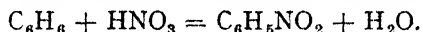
Cane-sugar is oxidized to oxalic acid:



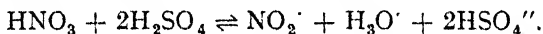
### Nitrating Action of Nitric Acid

Nitric acid reacts with a great many organic compounds, often merely oxidizing them to carbon dioxide and water. For example, if concentrated nitric acid be poured on heated sawdust, the mass often bursts into flame. If a dish of fuming nitric acid be placed in a basin in the bottom of a glass cylinder, and a little turpentine be added from a pipette, the turpentine will burst into flame. Glowing charcoal continues to burn when plunged into the acid.

But it does not always act with such violence, and in many cases causes the replacement of one or more hydrogen atoms of the organic compound by the  $-\text{NO}_2$  radical, which is known as the **nitro-group**. This process is known as **nitration** and is of great theoretical and practical importance. Thus, benzene is converted into nitrobenzene by a mixture of concentrated nitric and sulphuric acids:



Nitration has been shown to take place through the action of the  $\text{NO}_2^+$  ion; in presence of concentrated sulphuric acid it is believed that ionization takes place according to the equation



( $\text{H}_3\text{O}^+$  is the form in which the hydrogen ion is believed to occur as a rule—cf. page 269.)

### § 23 Action of Nitric Acid on Metals

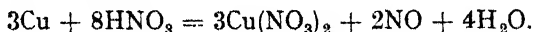
Nitric acid attacks all metals under appropriate conditions, except gold, platinum, iridium, titanium, tantalum and rhodium. Chromium and iron, however, are rendered *passive* by acid of a certain strength (pages 866 and 916); while tin, arsenic, antimony, tungsten and uranium are changed into their oxides and the other metals give nitrates.

But as a rule, the reaction is complicated by the simultaneous occurrence of oxidation and the normal acid reaction. In consequence, hydrogen is not evolved by the action of nitric acid on metals except when cold very dilute nitric acid acts upon magnesium or manganese, and even then the conditions have to be very carefully adjusted. In all other cases, one or other of the many possible reduction products of the acid is evolved, the nature of which depends upon the metal and

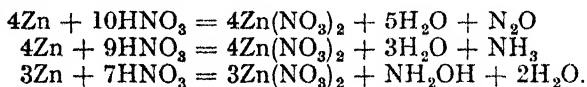
the conditions. Thus, copper, silver, bismuth and mercury give mainly nitrogen peroxide (page 464) with the concentrated acid:



and nitric oxide (page 459) with the dilute:

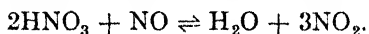


Iron, zinc, and cadmium, however, give mainly nitrous oxide (page 457) with the dilute acid, but with more concentrated acid may yield ammonia or hydroxylamine:



The ammonia, of course, reacts with excess of nitric acid to form ammonium nitrate. In certain circumstances, hyponitrous acid (page 456), or nitrogen, may also be formed by the action of nitric acid on a metal.

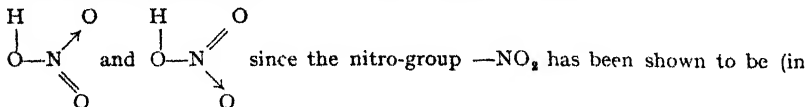
The precise mechanism of these reactions is still obscure but it may be noted that the metals which give mainly nitrogen peroxide with concentrated nitric acid (copper, silver, bismuth and mercury) are below hydrogen in the electrochemical series and so do not liberate hydrogen from other dilute acids. It may be, therefore, that the first action of dilute nitric acid on copper, for example, is the direct oxidation of the metal to copper oxide (with consequent reduction of the nitric acid) followed by salt formation by the metallic oxide and excess acid. This view is supported by the fact (W. H. Veley, 1890) that these metals have no action on cold dilute nitric acid unless a trace of nitrous acid or a lower nitrogen oxide is present, since nitrous acid oxidizes more readily than nitric acid. The formation of nitrogen peroxide when warm concentrated nitric acid reacts with copper may then be due to the oxidation of the nitric oxide first formed by more nitric acid.



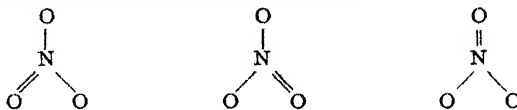
Iron, zinc and cadmium, on the other hand, are metals which, standing above hydrogen in the electrochemical series, do liberate hydrogen from dilute acids so that it is possible that, when they react with nitric acid, hydrogen is first formed; which then reduces more of the acid to hyponitrous acid, hydroxylamine or ammonia.

#### Formula

Nitric acid is now represented as a resonance hybrid (page 159) of the two forms



effect) symmetrical. The nitrate ion is triangular in shape and so is represented as a resonance structure embodying the three forms



The nitronium ion is probably linear with the structure  $\text{O} = \overset{+}{\text{N}} = \text{O}$ .

### § 24 Uses of Nitric Acid

Nitric acid finds many applications both in the laboratory and in industry. In the former, it is frequently employed as an oxidizing agent as, for example, the preparation of metallic oxides, oxyacids, and in the oxidation of ferrous to ferric salts in qualitative analysis. It is also a constituent of aqua regia (page 540) and is an important reagent in organic chemistry both for oxidation and nitration.

Industrially nitric acid is used in large quantities for the production of explosives, e.g., T.N.T. (trinitrotoluene); the manufacture of many nitro-compounds, for use as intermediates in the dye industry; in the production of celluloid, collodion and of silver nitrate for photographic and other purposes. It is also employed for cleaning metals (e.g., before electroplating) and for etching designs on copper. It is also an essential raw material for the production of many modern plastics and lacquers.

Some rocket propellants now employ 100 per cent nitric acid as one constituent of the fuel (cf. page 328).

### § 25 Detection and Determination of Nitric Acid

Nitric acid and nitrates are usually detected by the *brown-ring test*. The material to be tested is mixed with excess of concentrated sulphuric acid and cooled. Ferrous sulphate solution is then poured carefully down the side of the test-tube, so as to form a layer on the surface of the sulphuric acid. A brown ring, or layer, at the junction of the two liquids indicates the presence of a nitrate. This is due to the formation of nitric oxide through the reduction of the nitrate by some of the ferrous sulphate. This nitric oxide then forms the dark-coloured double compound,  $\text{FeSO}_4 \cdot \text{NO}$  (page 461), with more of the ferrous sulphate.

The brown-ring test is not always satisfactory; bromides and iodides interfere on account of the liberation of halogen and it is not trustworthy if chromates, sulphites, thiosulphates, iodates or cyanides are present. An alternative is to make use of Devarda's alloy (see below) as a qualitative test. Ammonium salts must be tested for first and, if present, the ammonia removed by boiling with sodium hydroxide solution.

Another simple qualitative test for a nitrate is to treat with concentrated sulphuric acid and warm, and then to add copper turnings.

The formation of brown fumes of nitrogen peroxide indicates the presence of a nitrate.

The quantitative determination of nitric acid and nitrates is rather difficult. The free acid can, in absence of other acids, be titrated with standard alkali. The most usual means of estimation is the use of Devarda's alloy (page 426), which yields ammonia quantitatively when heated with a nitrate in strongly alkaline solution. The ammonia formed is distilled into standard acid (page 437).

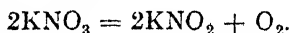
Nitrates can also be determined by shaking a solution containing the nitrate with concentrated sulphuric acid and mercury in a closed tube whereby the nitrate is reduced to nitric oxide. The volume of nitric oxide is accurately measured and the weight of nitrate radical present can be calculated. Since nitrites are also reduced to nitric oxide by this process it is necessary to remove or determine them separately.

Nitrates can also be determined gravimetrically by precipitation as the nitrate of an organic base known as *nitron*. The precipitate has the composition  $C_{20}H_{16}N_4 \cdot HNO_3$ .

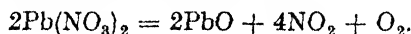
### § 26 Nitrates

The salts of nitric acid are known as **nitrates**. They are usually readily soluble in water and form well-defined crystals. When heated, nitrates decompose, and there are four types of decomposition according to whether a salt of (i) an alkali metal, (ii) a heavy metal, (iii) a noble metal, or (iv) ammonia is concerned.

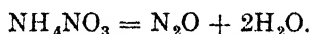
The nitrates of the alkali metals decompose on heating into the corresponding nitrite and oxygen:



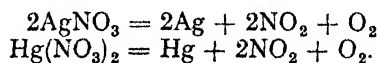
The nitrates of the heavy metals give oxygen, nitrogen peroxide (page 465) and the oxide of the metal, e.g.:



Ammonium nitrate decomposes on heating into nitrous oxide (page 457) and water:



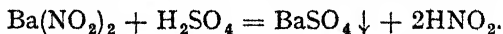
The nitrates of silver and mercury yield the metal on heating:



### § 27 Nitrous Acid, $HNO_2$

Nitrous acid is known only in the form of its salts and in dilute solution, on account of the readiness with which the free acid decomposes.

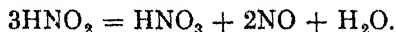
Dilute solutions of nitrous acid are formed when nitrogen trioxide (page 463) is dissolved in water at  $0^\circ$ , and by the addition to barium nitrite solution of the exact amount of dilute sulphuric acid theoretically required to precipitate the barium, the whole being cooled to  $0^\circ$ :



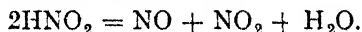
The precipitated barium sulphate can be filtered off, when a dilute solution of nitrous acid remains. Silver nitrite and dilute HCl can be used similarly.

### Properties

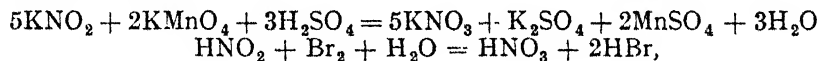
Nitrous acid is bright blue in colour, is very unstable and begins to decompose almost as soon as it is formed even at ordinary temperatures, nitric oxide being evolved and nitric acid formed:



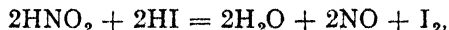
In concentrated solution or at higher temperatures, it breaks up into a mixture of nitrogen peroxide and nitric oxide:



Nitrous acid is very reactive and behaves either as a reducing agent, or as an oxidizing agent according to the circumstances. Thus, on the one hand, it reduces permanganates, dichromates, chlorine and bromine, e.g.:

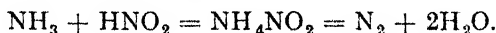


the former reaction serving for its volumetric determination. On the other hand it oxidizes hydriodic acid to iodine:



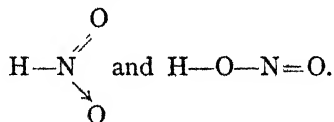
and reducing agents such as sulphur dioxide and stannous chloride are also oxidized by it.

Nitrous acid reacts with ammonia and substances (mostly organic) containing the  $-\text{NH}_2$  radical, eliminating the nitrogen of both substances as the free element, e.g.:

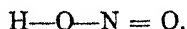


### Formula

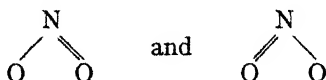
Two formulae have been suggested for nitrous acid, viz.:



The evidence available, some of it drawn from organic chemistry, indicates the existence of derivatives of both forms. There is no evidence to support the existence of both forms in equilibrium in the free acid which is probably:



The nitrite ion has a triangular structure and is probably a resonance hybrid of

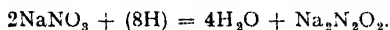


### Nitrites

The salts of nitrous acid are called **nitrites**. They are mostly very soluble salts, the only important exception being silver nitrite which is only sparingly soluble. Complex nitrites are known, some of which are noteworthy, e.g., the cobaltinitrites which are used in analysis.

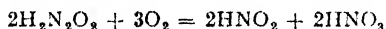
### § 28 Hyponitrous Acid, $\text{H}_2\text{N}_2\text{O}_2$

Hyponitrous acid and hyponitrites are obtained by the reduction of nitrites. When a solution of potassium or sodium nitrite or nitrate is treated with a solution of metallic sodium in mercury—sodium amalgam—the hydrogen liberated reduces the nitrite or nitrate, forming a new salt—**sodium hyponitrite**

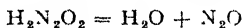


The alkaline solution can then be neutralized by acetic acid, and when silver nitrate is added, a yellow precipitate of **silver hyponitrite**,  $\text{Ag}_2\text{N}_2\text{O}_2$ , is formed. By treating silver hyponitrite, suspended in dry ether, with a solution of hydrogen chloride in dry ether, and evaporating the clear solution, white deliquescent crystalline plates are obtained. This is **hyponitrous acid**. The solid is very unstable and is liable to explode even below  $0^\circ$ .

It decomposes slowly when exposed to the air, giving nitrous and nitric acids:



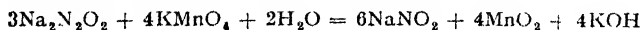
but boiling its aqueous solution causes the formation of nitrous oxide.



Hyponitrites are oxidized to nitrates by acid potassium permanganate solution:

$$5\text{Na}_2\text{N}_2\text{O}_2 + 8\text{KMnO}_4 + 12\text{H}_2\text{SO}_4 = 10\text{NaNO}_3 + 8\text{MnSO}_4 + 4\text{K}_2\text{SO}_4 + 12\text{H}_2\text{O}$$

and to nitrites by alkaline potassium permanganate:



Hyponitrites are not affected by reducing agents.

It is a dibasic acid, the lowering of the freezing point of the aqueous solution of the acid and the molecular weights of organic derivatives suggests that its formula is:





### § 29 Oxides of Nitrogen

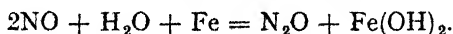
There are five well-established oxides of nitrogen, viz.:

Nitrous oxide,  $N_2O$ ;  
 Nitric oxide,  $NO$ ;  
 Nitrogen trioxide,  $N_2O_3$ ;  
 Nitrogen peroxide,  $NO_2 \rightleftharpoons N_2O_4$ ;  
 Nitrogen pentoxide,  $N_2O_5$ .

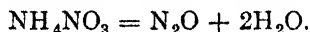
Others, such as  $NO_3$ , have been reported but their existence is doubtful.

### § 30 Nitrous Oxide, $N_2O$

Nitrous oxide was discovered by J. Priestley (1772), who made it by reducing nitric oxide with moist iron filings:



It is usually prepared from ammonium nitrate which yields the gas when heated:



The experiment is carried out by means of the apparatus indicated in Fig. 23.14. A convenient quantity of ammonium nitrate is placed in

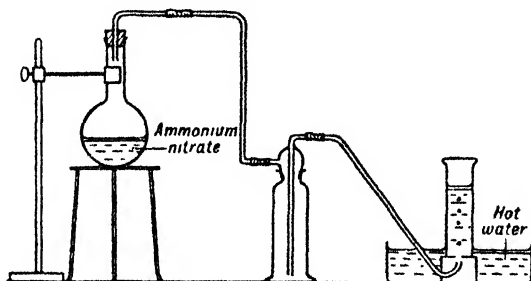


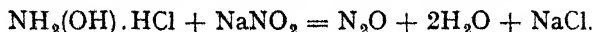
FIG. 23.14.—Preparation of Nitrous Oxide

the round-bottomed flask and heated, care being taken to avoid heating too strongly which causes explosive decomposition. The gas is sometimes collected over hot water on account of its perceptible solubility in cold. But it is then very moist and, in fact, can perfectly well be collected over cold water. As thus prepared, nitrous oxide may contain traces of nitric oxide and chlorine (from the ammonium chloride sometimes present in ammonium nitrate). These may be removed by washing with ferrous sulphate solution and sodium hydroxide.

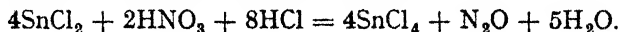
A mixture of sodium nitrate and ammonium sulphate or chloride can be used as a source of nitrous oxide; in this case, although evolution of gas takes place more slowly, it is more uniform and the risk of explosion is removed.

Q\*

Pure nitrous oxide is obtained by mixing solutions of hydroxylamine hydrochloride and sodium nitrite and warming gently:



Nitrous oxide can also be prepared by heating a mixture of stannous chloride with hydrochloric acid and a little nitric acid, when the reaction occurs as represented by the equation:



### Properties

Nitrous oxide is a colourless gas with a faint smell. 100 volumes of water, at 760 mm. pressure, dissolve 130 volumes of the gas at 0°; and 63 ml. at 20°. The aqueous solution has a sweetish taste. The gas condenses to a colourless limpid liquid at 0° under a pressure of 30 atmospheres. M. Faraday liquefied the gas in 1823. Liquid nitrous oxide can be purchased in steel cylinders. The liquid boils at  $-89.5^\circ$ , and freezes to a snow-like mass when allowed to evaporate. The cubic crystals melt at  $-102.4^\circ$ .

Nitrous oxide resembles oxygen in its behaviour towards combustibles. A brightly glowing splinter bursts into flame when plunged into the gas. Ignited phosphorus, sulphur, etc., burn vividly in nitrous oxide gas. The burning body decomposes the nitrous oxide, unites with the oxygen, and leaves the nitrogen as a residue. (If sulphur be but feebly burning, its flame is extinguished when plunged into nitrous oxide, because the temperature is not high enough to decompose the gas.) It is therefore easy to mistake nitrous oxide for oxygen. One distinguishing test is to add a bubble of the suspected gas to nitric oxide (page 428); if brown fumes are produced the gas is oxygen. Nitrous oxide does not give brown fumes with nitric oxide.

When inhaled, nitrous oxide produces unconsciousness, and insensibility to pain. Hence it has long been used as an anaesthetic for small surgical operations, e.g., in dentistry. But owing to the unpleasant after effects sometimes produced, it is not used so much as formerly. If the inhalation be long continued, it may produce death; while if but small quantities are inhaled, it may produce a kind of hysteria, or intoxication. Hence the gas is sometimes called "laughing gas."

The formation of nitrous oxide is an endothermic reaction:



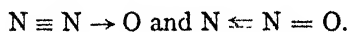
Nitrous oxide decomposes with an explosion if a fulminating cap be detonated in the gas. Nitrous oxide decomposes into its elements when heated; two volumes of the gas furnish two volumes of nitrogen and one volume of oxygen—three volumes in all.

In common with the other oxides of nitrogen, nitrous oxide is reduced when passed over red-hot copper:



### Composition and Formula

The gas, when decomposed by means of a heated iron wire in an apparatus such as that indicated in Fig. 23.15, yields its own volume of nitrogen. (Copper may be used similarly.) Since the nitrogen molecule is diatomic nitrous oxide must be  $N_2O_n$ , where  $n$  is still to be determined. Its vapour density has been found to be  $22(H_2 = 1)$ , hence its molecular weight is 44,  $n = 1$ , and its molecular formula is  $N_2O$ . It has been shown to have a linear and unsymmetrical structure, and is now formulated as a resonance hybrid (page 159) of the structures



### § 31 Nitric Oxide, NO

#### History

J. Priestley (1772) is generally regarded as the discoverer of nitric oxide; although J. Mayow (1669) made it by treating iron with nitric acid; and R. Boyle (1671) noted that it formed reddish-brown fumes in contact with air. J. B. van Helmont (c. 1600) knew the gas, although his descriptions seem to confuse it with carbon dioxide, probably because he had one name—gas sylvestre—for a number of different gases.

#### Preparation

Nitric oxide is formed from its elements at very high temperatures, a reaction already discussed in connection with the manufacture of nitric acid from the air (page 447).

It is also made on a large scale by the oxidation of ammonia for the production of nitric acid (page 448).

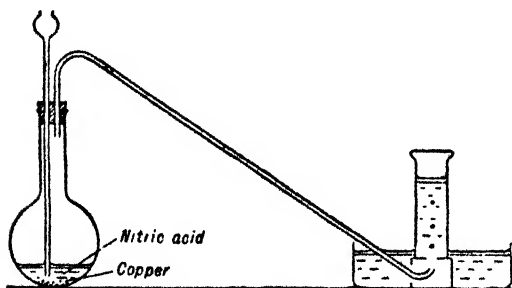


FIG. 23.16.—Preparation of Nitric Oxide

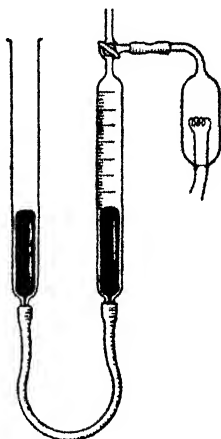
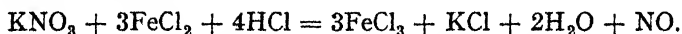


FIG. 23.15.—Composition of Nitrous Oxide

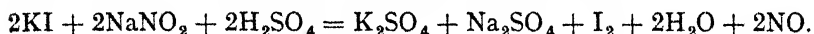
It is usually prepared in the laboratory by the action of nitric acid, specific gravity 1.2, upon metallic copper. Copper turnings are placed in a flask (Fig. 23.16). The flask is about one-fourth filled with water, and about the same volume of concentrated nitric acid

is added. A rapid evolution of gas occurs. The gas should be collected as soon as possible because when the reaction has been in progress some time, particularly if the temperature rises during the reaction, nitrous oxide and nitrogen may appear with the nitric oxide.

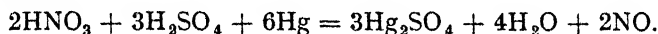
At first the flask is seen to be filled with brown fumes owing to the formation of nitrogen peroxide by combination of nitric oxide with the oxygen of the air originally in the flask (see below). Nitrogen peroxide is readily soluble in water, whereas nitric oxide is not; hence the flask soon "clears" and nitric oxide can be collected over water. A purer gas is obtained by reducing potassium nitrate with ferrous sulphate, acidified with sulphuric acid, or ferrous chloride acidified with hydrochloric acid:



According to L. W. Winkler (1889), highly pure nitric oxide can be made by dropping a 50 per cent solution of sulphuric acid upon a mixed solution of potassium iodide and sodium nitrite:



A very pure nitric oxide also results from the action of mercury on cold concentrated sulphuric acid to which nitric acid or a nitrate has been added:



The gas obtained from copper and nitric acid may be purified by absorption in cold, saturated ferrous sulphate solution (see below) from which it is recovered almost pure on warming. It still contains traces of nitrous oxide on account of the solubility of the latter in water. The specially pure nitric oxide used by Gray in determining the atomic weight of nitrogen (page 425) was purified in the following way. The crude gas was first passed through a large volume of water; then through concentrated aqueous potassium hydroxide solution; and dried by means of solid potassium hydroxide and phosphorus pentoxide. It was finally liquefied and fractionated twice in special apparatus, to remove nitrous oxide and nitrogen respectively.

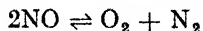
### Properties

Nitric oxide is a colourless gas, a little denser than air. When brought in contact with air, it immediately combines with the oxygen, forming brownish-red fumes of nitrogen peroxide. Hence it is not possible to describe the smell and the physiological action of this gas. If the two gases—nitric oxide and oxygen—be thoroughly dried, no combination occurs (cf. page 317).

Nitric oxide is difficult to liquefy. At  $-93.5^\circ$ , a pressure of 71.2 atmospheres is required to liquefy the gas. The liquid is colourless if air be excluded, otherwise the liquid may be tinted green or blue. The liquid boils at  $-151.8^\circ$ , and the white solid melts at  $-163.6^\circ$ .

Nitric oxide is very sparingly soluble in water at ordinary temperatures. It dissolves in a solution of ferrous sulphate. A "compound" of nitric oxide and ferrous sulphate appears to be formed. This imparts a dark brown colour to the solution. The "compound" is decomposed when heated to about 60°, and nitric oxide is evolved. It is not very clear if a true compound is formed between the nitric oxide and the ferrous salt, because its composition seems to vary with the temperature of formation. The maximum extent of the absorption corresponds with the formula  $\text{FeSO}_4 \cdot \text{NO}$ .

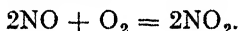
Nitric oxide is one of the most stable of the nitrogen oxides. Decomposition does not begin when it is heated until the temperature reaches 500° and is still slight at 900°. The reaction



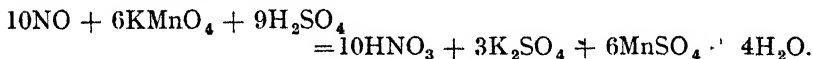
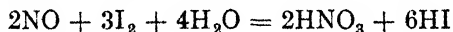
is reversible, as indicated on page 447, and at still higher temperatures, say, 3000°, only 4 per cent of the mixture of nitrogen and oxygen will combine to form nitric oxide.

Nitric oxide is not combustible, and it only supports combustion under special conditions, that is, when the temperature is raised sufficiently to decompose the gas. The flame of feebly burning phosphorus is extinguished, but if the phosphorus be burning vigorously, combustion is continued in the gas. Burning sulphur is extinguished, but if the sulphur be boiling when it is plunged in the gas combustion sometimes continues.

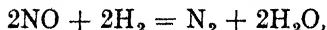
Nitric oxide is converted by oxidizing agents into nitrogen peroxide, or nitrates. The gas, as noticed previously, combines directly with oxygen in the cold forming nitrogen peroxide:



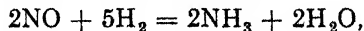
Other oxidizing agents usually form nitric acid, e.g.:



Nitric oxide reacts, however, with many reducing agents and is usually converted into nitrogen, but occasionally ammonia or nitrous oxide is formed. Thus, sparking with hydrogen gives nitrogen:



but if a mixture of nitric oxide and hydrogen be passed over a catalyst (such as platinum black), ammonia results:



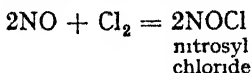
while with concentrated aqueous potassium hydroxide nitrous oxide is formed:



and with sulphurous acid (or sulphur dioxide in presence of water) nitrous oxide is also produced:



Nitric oxide readily forms addition products, e.g., with oxygen, and metallic salts as above, and also with the halogens:



### Formula

The formula of nitric oxide is determined by means of an apparatus such as that indicated in Fig. 23.17. A spiral of iron or nickel wire is strongly heated electrically in a measured volume of nitric oxide, thereby reducing it to nitrogen. After cooling, the nitrogen is found to occupy half the volume of the nitric oxide from which it is formed. That is, nitric oxide contains *half* its own volume of nitrogen and hence, by Avogadro's hypothesis, its molecular formula is  $\text{NO}_x$  where  $x$  has still to be found. The vapour density of nitric oxide has been found to be 15 ( $\text{H}_2 = 1$ ), hence its molecular weight is 30,  $x = 1$ , and the molecular formula is  $\text{NO}$ .

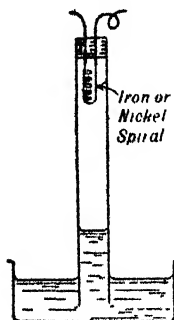


FIG. 23.17.  
Composition of  
Nitric Oxide

The gravimetric composition of nitric oxide was determined by Gray (1905) using the apparatus indicated in Fig. 23.18. It consisted of a combustion bulb, fitted with a ground stopper, carrying two thick platinum electrodes. Joined to the stopper was a stopcock and capillary glass tube, the latter being connected to the rest of the apparatus by a ground joint. The electrodes were connected inside the bulb to thick nickel wire leads which supported a small porcelain boat containing finely divided nickel. The boat had a fine platinum wire wound round its whole length and connected to the nickel leads so that the boat could be heated by connecting the electrodes to a source of electricity. The absorption bulb was connected by another ground joint and could be immersed in liquid air in a Dewar flask as shown. The combustion bulb was first completely evacuated and weighed. It was then filled with pure nitric oxide to a pressure of nearly 2 atmospheres and weighed again. The nickel in the boat was now heated for 15 minutes. After cooling, the combustion bulb was put into communication with the absorption bulb (which contained powdered coconut charcoal and which had been previously weighed) which was then immersed in liquid air. After 30 minutes, when all the nitrogen had been absorbed by the charcoal the bulbs were weighed again. The increase in the weight of the absorption bulb is the weight of nitrogen which was combined with a weight of oxygen given by the increase in the weight of the combustion bulb. Gray used his results to calculate the atomic weight of nitrogen (page 425).

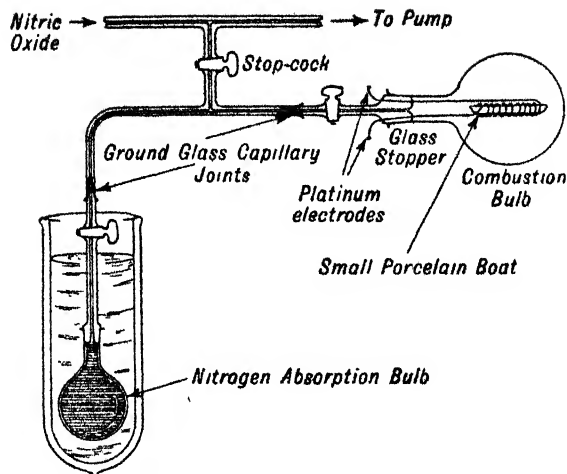
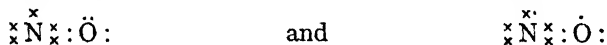


FIG. 23 18.—Gray's Apparatus  
(Adapted from *J. Chem. Soc.*, 1905)

The formula NO cannot be made to fit in with the accepted valencies of nitrogen and oxygen.

The ready way in which nitric oxide unites with other elements by direct addition shows that nitric oxide is unsaturated; but it is difficult to understand why it does not form double molecules ( $N_2O_2$ ). Various electronic formulae have been proposed but the fact that the molecule contains an odd number of electrons is a difficulty. Pauling considers that the nitric oxide is best represented as a resonance hybrid of



which he thinks may be equivalent to the formation of a peculiar 3-electron bond, thus:



This, it is thought, may be the explanation of the absence of any tendency to form double molecules of  $N_2O_2$ .

### § 32 Nitrogen Trioxide, $N_2O_3$

When a mixture of nitric oxide and nitrogen peroxide is passed through a tube cooled to about  $-30^\circ$ , a more or less impure form of nitrogen trioxide— $N_2O_3$ —condenses to a bluish liquid. As soon as the temperature rises, the liquid dissociates, nitric oxide escapes, and leaves a residual yellow liquid of nitrogen peroxide. The melting-point curve of mixtures of nitric oxide and nitrogen peroxide indicates the formation of a compound  $N_2O_3$  melting at  $-102^\circ$ .

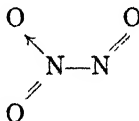
The trioxide is also produced by the direct union of solid nitrogen peroxide with nitric oxide; and by the action of oxygen on liquid nitric oxide; and as a green flocculent powder, resembling chromic hydroxide, when a series of electric discharges are passed through liquid air. The trioxide, not the peroxide, appears to be formed when nitric oxide unites with oxygen at temperatures below  $-100^{\circ}$ .

A gas containing a considerable proportion of nitrogen trioxide can be obtained by the action of arsenic trioxide on 60 per cent nitric acid; the nitrogen trioxide can be condensed out of the mixture by cooling. The composition of nitrogen trioxide has been established by passing the products of its decomposition over heated copper, and weighing the copper oxide and the nitrogen.

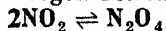
Nitrogen trioxide derives some interest and importance from the fact that, theoretically, it is the anhydride of nitrous acid. When dissolved in water it gives a mixture of nitric and nitrous acids, but with alkali it combines to give only the nitrite.

According to H. B. Baker (1907), if the liquid be thoroughly dried, it vaporizes without dissociation, forming a gas which has a vapour density never below 38 ( $H_2 = 1$ ), but generally much above that number which corresponds to the formula  $N_2O_3$ . If this be confirmed, it is the only direct evidence we have of the existence of the gaseous nitrogen trioxide. The freezing-point method of determining the molecular weight in acetic acid furnished W. Ramsay (1888) with numbers between 80.9 and 92.7—theory for  $N_2O_3$  requires 76.02. Hence the liquid is partly polymerized. B. M. Jones (1914) concluded that the dry liquid consists mainly of  $N_4O_6$  molecules, which on vaporization give  $N_2O_3$ ,  $NO_2$  and  $NO$  in equal volumes. Many reactions formerly said to yield the trioxide really give a mixture of nitric oxide and nitrogen peroxide.

The structure of nitrogen trioxide is still not certain; it is thought most likely to be



### § 33 Nitrogen Dioxide, Nitrogen Tetroxide, Nitrogen Peroxide,\*



#### History

As indicated in discussing nitric oxide, R. Boyle (1671) knew that nitric oxide forms brown fumes in air, and these brown fumes are

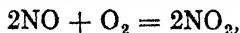
\* Nitrogen peroxide is the name commonly applied to the gas obtained at ordinary temperatures, and which is, as explained below, a mixture of two molecular species,  $NO_2$  and  $N_2O_4$ , in equilibrium. A more satisfactory nomenclature is to call  $NO_2$  *nitrogen dioxide*, and  $N_2O_4$  *nitrogen tetroxide*.



mentioned in alchemical writings as *the blood of the salamander*. Since nitrogen peroxide is always formed during the preparation of nitric acid, nitrogen peroxide must have been recognized as a gas whenever nitric acid was made. J. L. Gay-Lussac (1816) first made its composition clear.

### Preparation

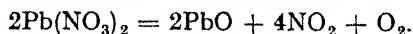
Nitrogen peroxide results when nitric oxide and oxygen are mixed:



but this is an interesting mode of formation rather than a practicable method of preparation. It also results from the action of concentrated nitric acid on copper:

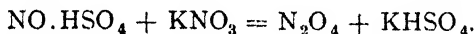


It can be prepared conveniently in small quantities by heating the nitrate of a heavy metal, *dry* lead nitrate being the one most usually employed:



It is then separated from the oxygen formed at the same time by passing the mixed gases through a U-tube immersed in a freezing mixture (Fig. 23.19). The nitrogen peroxide condenses to a yellow liquid, while the oxygen escapes. (If any moisture be present, the liquid is green.)

The best method of preparation is said to be to heat nitrosyl hydrogen sulphate (page 468) with dry potassium nitrate (Park and Partington, 1924):



It is also often prepared by the action of arsenic trioxide on ordinary concentrated nitric acid (sp. gr. 1.42). When these two substances are warmed together, the nitric acid is reduced. As the reaction proceeds the concentration of the nitric acid diminishes, and consequently the nature of the reduction product changes. As a result a mixture of oxides of nitrogen containing a considerable proportion of nitrogen peroxide is formed. The gases, as before, are led through a U-tube immersed in a freezing mixture. When evolution of gas has ceased, a current of air or oxygen is passed through the liquid until it becomes yellowish-brown to remove or oxidize any nitrogen trioxide present.

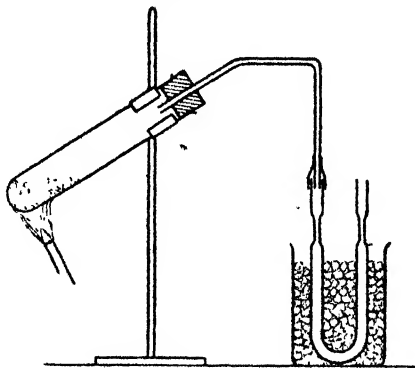


FIG. 23 19  
Preparation of Nitrogen Peroxide

### Properties

Nitrogen peroxide is a brown gas, the colour of which deepens on heating, owing to the larger proportion of  $\text{NO}_2$  molecules present at higher temperatures. It has a strong and pungent odour and an acid taste and is very poisonous. When cooled it readily condenses to a yellow liquid (b.p.  $21.3^\circ$ ) and finally freezes to a colourless solid (m.p.  $-9.3^\circ$ ).

The action of heat on nitrogen peroxide is of interest. On heating the liquid from about the melting point, as the temperature of the liquid rises, it begins to acquire a pale greenish-yellow tint, which becomes deeper and deeper, until at  $10^\circ$  the liquid is distinctly yellow; at  $15^\circ$ , orange; and at  $21.3^\circ$  the liquid boils and forms a reddish-brown vapour. As the temperature is raised the colour of the vapour becomes deeper and deeper until, at  $40^\circ$ , it is dark chocolate-brown, and almost opaque; at  $140^\circ$  the vapour is almost black. On cooling the vapour, the same changes occur in the reverse order.

The vapour density of the gas at ordinary temperatures is intermediate between the values corresponding to the formulæ  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  respectively, as seen from the following table.

TABLE XXXII.—VAPOUR DENSITY OF NITROGEN PEROXIDE

Temperature	Vapour density (Hydrogen = 1)	Percentage of $\text{NO}_2$ molecules
$26.7^\circ$	38.3	20.1
$60.2^\circ$	30.1	52.8
$100.1^\circ$	24.3	89.3
$135.0^\circ$	23.1	99.1
$140^\circ$	23.0	100.0

The figures in the last column are obtained as follows:

Let  $n$  = number of molecules of  $\text{N}_2\text{O}_4$  which would be present if no dissociation had taken place and

let  $x$  = number of molecules of  $\text{N}_2\text{O}_4$  which have dissociated.

Then  $(n - x)\text{N}_2\text{O}_4 \rightleftharpoons 2x\text{NO}_2$

$\therefore$  Total number of molecules present in the vapour

$$= n - x + 2x = n + x$$

$\therefore$  According to Avogadro's Hypothesis

$$\frac{\text{observed volume of the vapour}}{\text{volume of vapour if undissociated}} = \frac{n + x}{n}$$

The volumes of the same mass of two vapours are inversely proportional to their densities (since density = mass/volume)

$$\therefore \frac{\text{vapour density of undissociated } \text{N}_2\text{O}_4}{\text{observed vapour density}} = \frac{n + x}{n}$$

so that the fraction of molecules which have dissociated

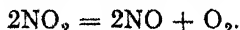
$$= \frac{x}{n} = \frac{\text{vapour density of undissociated } \text{N}_2\text{O}_4}{\text{observed vapour density}} - 1$$

Taking now as an example the fact that the vapour density is 38.3 at 26.7°, the fraction dissociated

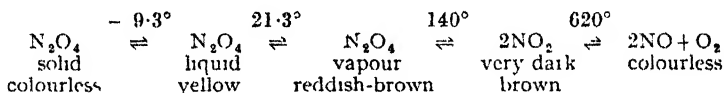
$$= \frac{46}{38.3} - 1 = \frac{7.7}{38.3} = 0.201$$

i.e., the gas is 20 per cent dissociated.

When the temperature is above 140° the density decreases still further and gas begins to grow paler again. This is because an appreciable number of the dark brown molecules of  $\text{NO}_2$  begin to dissociate into a colourless mixture of nitric oxide and oxygen:

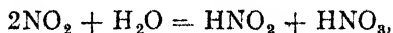


This dissociation is complete at 620°. The reverse changes take place on cooling. The action of heat on nitrogen peroxide may therefore be represented by the equations:

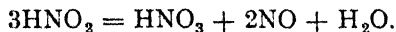


Nitrogen peroxide is not combustible, and it may extinguish the flame of a taper. Phosphorus, sulphur, and carbon, if burning vigorously, may continue burning in the gas, but only when the temperature of combustion is sufficiently high to decompose the gas. Nitrogen peroxide is an energetic oxidizing agent. Phosphorus, carbon, potassium, mercury, copper, etc., when heated in the gas, are oxidized, while the gas is decomposed. The gas liberates iodine from potassium iodide; but it reduces permanganates, forming nitric acid. Nitrous oxide, indeed, is the only gaseous nitrogen oxide which does not decolorize aqueous solutions of potassium permanganate. Nitrogen peroxide resembles ozone and hydrogen peroxide in some of its reactions.

Nitrogen peroxide is decomposed by water. At low temperatures, a mixture of nitric and nitrous acids is formed,



for which reason it is called "a mixed anhydride." The solution of mixed acids is unstable, unless very dilute, the nitrous acid decomposing thus:

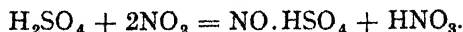


This reaction is an important step in the process for the synthesis of nitric acid from the air (page 449).

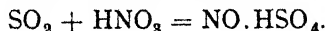
When water is treated with an excess of nitrogen peroxide, the solution passes through a series of colour changes—blue, green, orange.

This is due to the gradual solution of the nitrogen peroxide in the nitric acid formed as just indicated. If sufficient water be present, the solution finally becomes colourless.

Nitrogen peroxide dissolves in concentrated sulphuric acid forming **nitrosyl hydrogen sulphate**, formerly known as **nitro-sulphuric acid** and nitric acid:



Nitrosyl hydrogen sulphate is, however, best prepared by passing sulphur dioxide into cold fuming nitric acid

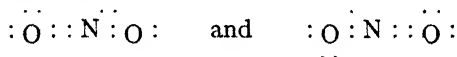


This compound is sometimes known as *chamber crystals* since it is formed in the chamber process for sulphuric acid manufacture if the supply of steam or water be insufficient (page 499).

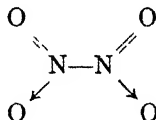
### Composition and Formula

When nitrogen peroxide is decomposed with copper, or nickel, as in the similar investigation of nitric oxide (page 462) the results indicate a percentage composition corresponding to the empirical formula  $\text{NO}_2$ . Vapour density measurements, as shown above, point to an equilibrium mixture of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ .

The structures to be assigned to nitrogen peroxide are still a matter for discussion. One formula for  $\text{NO}_2$  which has been widely used is  $\text{O} = \text{N} \rightarrow \text{O}$  but according to Pauling it is a resonance hybrid, similar to nitric oxide (page 463), with a three-electron bond:



At present the formula



is preferred for the  $\text{N}_2\text{O}_4$  molecule.

### § 34 Nitrogen Pentoxide

Nitrogen pentoxide is obtained by adding to pure, well-cooled nitric acid contained in a distilling flask twice its weight of phosphorus pentoxide. The temperature is raised to  $60^\circ$ – $70^\circ$  and the nitrogen pentoxide distilled in a current of ozonized oxygen, into a series of well-cooled wash-bottles.

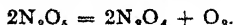


Nitrogen pentoxide also results from the action of ozone on nitrogen peroxide and from that of chlorine on dry silver nitrate:



**Properties**

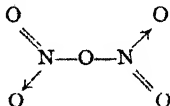
Nitrogen pentoxide is obtained as above in the form of white crystals. At ordinary pressure it sublimes without melting; its melting point is, however, given as 30°. Above this temperature it decomposes; when rapidly heated it explodes.



It reacts with water, producing nitric acid, and hence it may be regarded as nitric anhydride:

**Composition**

Analysis, by means of copper, indicates the empirical formula  $\text{N}_2\text{O}_5$ . Its vapour density corresponds to this formula and its structure is thought to be best represented as

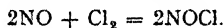
**§ 35 Other Oxides of Nitrogen**

When nitric oxide is passed through liquid air, or liquid oxygen, a green solid is formed which has been assumed to be **nitrogen hexoxide**,  $\text{NO}_3$  or  $\text{N}_3\text{O}_6$ . It has also been obtained by the action of a silent discharge on a mixture of nitrogen peroxide and oxygen.

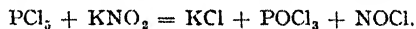
More recently (1925) it has been suggested that this green solid is  $\text{N}_3\text{O}_4$ , but the nature of this substance is still uncertain.

**§ 36 Nitrosyl Chloride, NOCl**

Nitrosyl chloride results from the slow union of nitric oxide and chlorine at ordinary temperatures. The reaction is considerably accelerated by the presence of charcoal.



It can also be obtained by the action of phosphorus pentachloride on potassium nitrite:



It is also formed from aqua regia (page 540).

Nitrosyl chloride is an orange-yellow gas which condenses at  $-5.5^\circ$  to an orange-coloured liquid; it freezes at  $-64.5^\circ$  to lemon crystals. It is decomposed by water into nitrous and hydrochloric acids.



It has no action on gold and platinum, but attacks mercury, forming mercurous chloride and nitric oxide; it also forms double compounds like  $\text{SnCl}_4 \cdot \text{NOCl}$ ;  $\text{FeCl}_3 \cdot \text{NOCl}$ , etc.

## CHAPTER 24

### SULPHUR

As when that devilish iron engine, wrought  
In deepest hell, and framed by furies' skill,  
With windy nitre and quick sulphur fraught,  
And ramm'd with bullet round, ordain'd to kill,  
Conceiveth fire.—EDMUND SPENSER

#### § 1 History and Occurrence

THE element sulphur has been known from the beginning of history. It is mentioned in the Bible and in Homer. It was placed among the elements by Lavoisier, but for some time previously it was regarded as "the principle of fire." The name is derived from the Sanscrit *sulveri* through the Latin *sulphurium*.

Among the Greeks and Romans sulphur was used for fumigation, and the vapours of burning sulphur were employed for bleaching clothes. It was used medicinally in the Middle Ages and is a constituent of gunpowder which was introduced into Europe about the beginning of the fourteenth century (page 642).

#### Occurrence

Sulphur is widely distributed in nature both as free and as combined sulphur. Deposits of free or native sulphur occur in volcanic districts, Iceland, Italy (Romagna, Marken, Tuscany, Campania, and Calabria), Sicily (chiefly on the southern watershed), Greece (Island of Milo), Russia, Austria, Hungary (Radoboj and Swoscowice), South France, Spain, Asia Minor, Persia, India, Palestine, Algeria, Morocco, Japan (Sulphur Island), New Zealand (White Island, etc.), United States (Louisiana, Oregon, Utah, Nevada, Wyoming, Texas), Mexico (Popocatepetl), Chile, Peru, etc. These districts are on or not far from the dotted line, Fig. 24.1, which indicates the distribution of regions of volcanic activity.

There are two main types of native sulphur: (1) *The solfataric type*\* found in lava fissures and in extinct volcanic vents (Japan, Mexico). Deposits of this type are forming at the present day in volcanic districts from the mutual action of hydrogen sulphide and sulphur dioxide which occur among volcanic gases.

(2) *The gypsum type*. The sulphur appears to have been liberated from gypsum by the reducing action of bituminous matters found

\* Solfatara—a volcanic vent or volcanic area which gives off sulphurous vapours, steam, etc., and which probably represents the last stages of volcanic activity.

associated with the gypsum. Calcium sulphide is probably formed from the sulphate, and this, by the action of water and carbon dioxide, forms sulphur, calcium carbonate and hydrogen sulphide. The Sicilian deposits and perhaps the more important sulphur deposits are of this type.

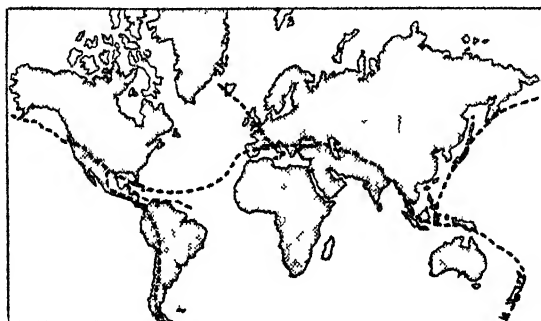


FIG. 24.1 - Imaginary Lines showing Chief Regions of Volcanic Phenomena and Occurrence of Sulphur Deposits

Many important metallic ores are **sulphides**, that is compounds of sulphur with one or more metals. Thus, *galena* (lead sulphide,  $\text{PbS}$ ), *zinc blende* (zinc sulphide,  $\text{ZnS}$ ), *cinnabar* (mercury sulphide,  $\text{HgS}$ ), *stibnite* (antimony sulphide,  $\text{Sb}_2\text{S}_3$ ), *copper pyrites* ( $\text{Cu}_2\text{S}$ ,  $\text{Fe}_2\text{S}_3$ ), iron pyrites (iron sulphide,  $\text{FeS}_2$ ), etc. Some important **sulphates** also contain sulphur, e.g., *gypsum* (calcium sulphate,  $\text{CaSO}_4$ ), *heavy spar* (barium sulphate,  $\text{BaSO}_4$ ), etc.

Sulphur occurs in many organic compounds, and in animal and vegetable products: onions, garlic, mustard, horseradish, hair, many oils, eggs, proteins, etc. Hydrogen sulphide and its oxidation products are found in the water of many sulphur springs. Sulphur also occurs as a constituent of coal (cf. page 382) and petroleum.

## § 2 Manufacture of Sulphur

The "sulphur earth" in Sicily occurs in lodes mixed with limestone and gypsum. The amount of sulphur in "workable" ore varies from 8 up to about 25 per cent. The sulphur is separated by heating the ore, and allowing the molten sulphur to flow away from the mineral impurities. This is effected by stacking the ore on the sloping floor of a circular kiln without a permanent roof. The kilns are called *calcaroni*.

A portion of the sulphur acts as fuel, and melts the remainder which collects at the lowest point of the inclined bottom of the kiln.

About one-third of the sulphur is lost in the *calcarone* system of

extraction. It is, however, cheaper to use the sulphur as a fuel than to import coal. The loss, however, is excessive even then, and in consequence the calcarone method is being displaced by more economical kilns—Gill's kilns—which are worked in sets.

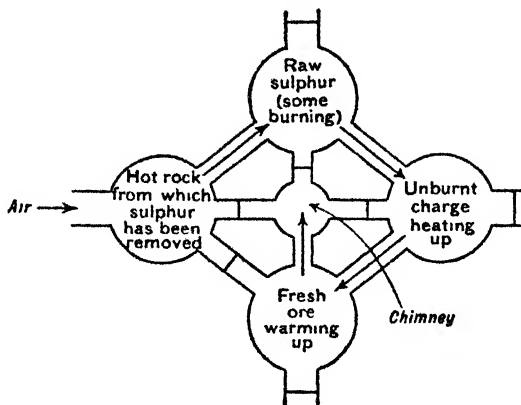


FIG. 24.2—Gill Regenerative Sulphur Furnace

Fig. 24.2 shows a plan of a set of such kilns which consist of a series of chambers with domed roofs. The air is admitted into a chamber which contains hot "rock" from which the sulphur has melted out, and thus the air is warmed. It then passes to a chamber containing hot raw sulphur, some of which burns and so melts out the remaining sulphur in the contents of this chamber. The hot gases then pass through several other kilns charged with raw sulphur rock which is thus heated up, and so loss of heat is reduced to a minimum.

The American sulphur deposits, which are now the principal source of the world's sulphur, occur at a depth of some 500 feet underneath strata of clay, limestone, etc. Their extraction by ordinary mining is impossible, both on account of the waterlogged nature of the strata concerned, and of the considerable quantities of hydrogen sulphide and sulphur dioxide which occur and make it impossible for men to work in shafts sunk into the sulphur-bearing stratum.

The problem was solved by Frasch who developed the method now in use, consisting of forcing superheated water into the sulphur bed thus melting the sulphur, and forcing it through a tube to the surface in the form of a kind of foam produced by a stream of air bubbles. The method is illustrated in Fig. 24.3.

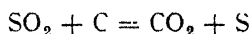
The crude sulphur from the kilns—also called "brimstone"—is graded and put on the market. It may be afterwards purified by distillation from a retort which opens into a large brickwork chamber. The sulphur vapour condenses in the chamber. The first lot of vapour sublimes as a light powder on the walls. The powder is called *flowers*



of sulphur. As the condensing chamber gets hot, the condensed sulphur melts and collects on the floor as a liquid which is drawn off from time to time and cast in large wooden moulds—*rock sulphur*; or in cylindrical wooden moulds—*roll sulphur*.

The sulphur produced by the Frasch process is of a high degree of purity and for most purposes does not need any further purification. It can be further purified by distilling it repeatedly in a current of carbon dioxide.

Sulphur can now be produced from the sulphur dioxide contained in the waste gases of metallurgical operations by reducing the dioxide back to sulphur. The reduction is effected by means of carbon in the form of coke, the reaction:



taking place rapidly at  $1100^\circ$ , at which temperature it is practically complete. The reaction is exothermic and does not require any external heat for its maintenance, when once the required temperature has been reached.

This process is likely to become increasingly important, since the turning to waste of the sulphur dioxide from metallurgical operations has often been due to the greater difficulty and greater cost of transporting sulphuric acid. Now that the sulphur of the waste gases can be recovered as such, this obstacle is removed. This procedure cannot be applied economically to a gas mixture containing so small a proportion of sulphur dioxide as the average in smelter gas (5 per cent or less). A preliminary concentration of the gas is therefore necessary. This is effected by absorption in a solution of basic aluminium sulphate; the sulphur dioxide is then recovered by heating the solution. The residual basic aluminium sulphate solution can then be used again.

Some smelter gases which are richer in sulphur dioxide can be reduced to sulphur without a preliminary concentration by means of a "reducing gas" obtained by passing the smelter gas plus air over red-hot coke. This gas together with more of the original smelter gas is passed over a special catalyst.

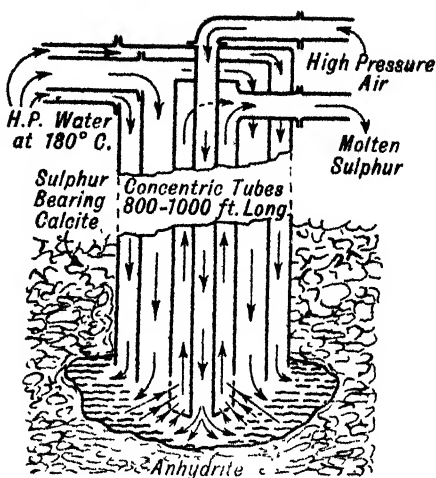


FIG. 24.3.—Frasch Pump

### § 3 Allotropy of Sulphur

Sulphur is known in a large number of allotropic forms, and the exact relationship existing between them is complex, and in some cases uncertain.

Several clearly defined and distinct solid forms are known, viz.,

**Rhombic**, octahedral or  $\alpha$ -sulphur, or  $S_1$ .

**Monoclinic**, prismatic or  $\beta$ -sulphur, or  $S_{11}$ .

**Amorphous** sulphur.

**Colloidal**, or  $\delta$ -sulphur.

In addition to these there have been described:

Plastic sulphur, which is a super-cooled liquid, and is probably a mixture of forms and not a true allotrope;

Nacreous sulphur, a crystalline form (see below), the exact nature of which seems still doubtful;

Colloidal sulphur, milk of sulphur, etc., which are composed of amorphous sulphur in various states of division.

Numerous crystalline modifications, e.g., tabular sulphur, Friedel's triclinic sulphur, Engel's rhombohedral sulphur, the precise nature of which in relation to the established forms is dubious.

Liquid sulphur also is now believed to consist of at least two forms, viz.:

$\lambda$ -sulphur, predominating at lower temperatures,

and  $\mu$ -sulphur, predominating at higher temperatures,

while a third liquid form  $S_\pi$  has also been postulated.

The vapour, too, appears to contain both  $S_8$  and  $S_2$  molecules in equilibrium and possibly  $S_4$  also.

### § 4 Sulphur and the Phase Rule

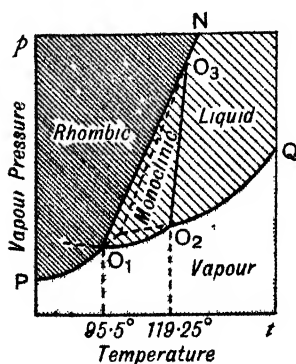


FIG. 24 4 — Phase Rule Diagram of Sulphur

The diagram (Fig. 24 4) illustrates the phase rule relationships of the two principal solid forms of sulphur.

By plotting the vapour pressure curve of rhombic sulphur at different temperatures, we get the curve  $PO_1$ , similarly, by plotting the vapour pressure curve of monoclinic sulphur, we get the curve  $O_1O_2$ , this variety of sulphur melts at  $119.25^\circ$ , however, by continuing the vapour pressure curve of the liquid, we get  $O_2Q$ . By plotting the transition points of rhombic sulphur at different pressures, we get the curve  $O_1O_3$ , and by plotting the melting point of monoclinic sulphur at different pressures, we get the curve  $O_2O_1$ . Monoclinic sulphur cannot exist at pressures higher than that represented by the point  $O_3$ . The continuation of the curve  $O_3N$  represents the effect of pressure on the melting point of rhombic sulphur.

The phase rule enables us to form a very clear

idea of the conditions of equilibrium. When the condition of the system is represented by a pressure and temperature corresponding with one of the three triple points— $O_1$ ,  $O_2$ ,  $O_3$ —the system is invariant, and any change in temperature or pressure will lead to the suppression of one of the three phases; points on one of the curves  $PO_1$ ,  $O_1O_2$ ,  $O_2O_3$ , etc.,  $\therefore$  represent univariant systems; and points in one of the three regions— $PQ$ ,  $QO_2N$ ,  $NO_1P$ —represent bivariant systems. It will of course be obvious that we are here dealing with the one component sulphur, and four possible phases—sulphur vapour and liquid, and rhombic and monoclinic sulphur—since an allotropic modification of an element is a true phase.

The metastable states, or states of false equilibrium, are interesting. The  $QO_2$  and the  $PO_1$  curves meet at a point corresponding with the temperature  $112.8^\circ$ . This is the melting point of rhombic sulphur. If the transformation of rhombic to monoclinic were very fast, it would be impossible to state the melting point of rhombic sulphur, because it would pass into the monoclinic form before a determination could be made.

The upward left-to-right slopes of the curves  $O_1O_2$  and  $O_2O_3$  correspond with the fact that the melting point of sulphur is raised by increasing pressures.

### § 5 Rhombic, Octahedral or $\alpha$ -Sulphur

The considerations discussed in the previous section indicate that it is this form which is stable at temperatures below  $95.5^\circ$ , so that this is the form in which sulphur is normally found. To get well-defined crystals, it is necessary to allow sulphur to crystallize from solution in, say, carbon disulphide. A sample of sulphur is ground up and shaken with carbon disulphide, filtered and the solution allowed to evaporate slowly in a crystallizing dish. Octahedral crystals slowly grow, and from transparent, amber-coloured crystals similar to those shown in Fig. 24.5. When heated to  $94.5^\circ$  they become opaque, owing to the formation of monoclinic sulphur. They have a density of 2.1 at  $20^\circ$  and when rapidly heated melt at  $112.8^\circ$ , since the transformation into monoclinic sulphur is so slow.

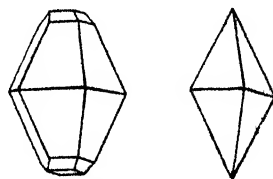


FIG. 24.5.  
Rhombic Sulphur Crystals

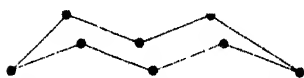


FIG. 24.6.—The Structure of Sulphur ( $S_8$ ) Molecules

The investigation of crystals of rhombic sulphur, by means of X-rays, has shown that it is composed of ' $S_8$ ' molecules arranged in the form of a puckered eight-membered ring as shown in Fig. 24.6.

### § 6 Monoclinic, Prismatic or $\beta$ -Sulphur

This form of sulphur, as can be seen from Fig. 24.4, is stable between  $94.5^\circ$  and  $119.25^\circ$ ; and is thus obtained by crystallization within this range of temperature. This is often done by melting sulphur and allowing it to solidify.

If 50 grams of sulphur be melted in a clay or porcelain crucible and the mass allowed to stand until a surface crust is formed, beautiful

long prismatic needle-like crystals of waxy yellow sulphur will be found to have grown on the walls of the crucible, and on the underside of the crust when the crust is pierced, and the still fluid sulphur is poured away.

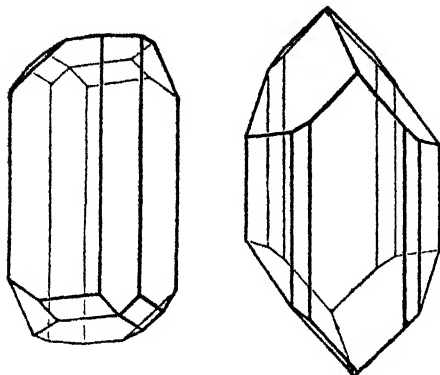
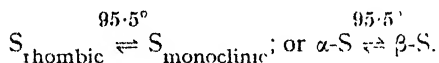


FIG 24 7.—Monoclinic Sulphur

Well-formed crystals of monoclinic sulphur can also be obtained by making a saturated solution of sulphur in boiling toluene (in which it is, however, only sparingly soluble) and allowing it to cool slowly. The crystalline form of monoclinic sulphur is shown in Fig. 24.7. Its density is 1.96.

Crystals made by either of the above methods, if allowed to stand for about a day, become light yellow, opaque, brittle, and crumble into

powder at the slightest touch. The grains of powder are small rhombic crystals of  $\alpha$ -sulphur. If the rhombic crystals be kept a few hours between  $108^\circ$  and  $112^\circ$ , they also become opaque and change to a friable crumbling mass of monoclinic prisms. The two reactions are thus reversible. Experiment shows that the monoclinic prisms are unstable below  $95.5^\circ$ , and slowly pass into the rhombic variety. The change is accelerated by wetting the monoclinic prisms with carbon disulphide, or by bringing the monoclinic sulphur into contact with a crystal of the rhombic variety. Conversely, the rhombic sulphur is unstable above  $95.5^\circ$ , and slowly passes into the monoclinic variety. The change is symbolized:



Hence,  $95.5^\circ$  is a transition temperature. When the range of stability of two allotropic forms of an element can be defined, as in the case of rhombic and monoclinic sulphur, by means of a transition point above which one form and below which the other is stable the element is said to exhibit **enantiotropy**. Where there is no transition point, so that one form is unstable at all temperatures, the phenomenon is described as **monotropy**. (Cf. phosphorus, page 816.)

The X-ray examination of monoclinic sulphur indicates the presence of the same molecular species as in rhombic sulphur so that the difference between the two forms is in the way the same ( $S_8$ ) molecules are built up into the different (rhombic or monoclinic) crystals.

### § 7 Plastic or $\gamma$ -Sulphur

If sulphur, heated to about  $350^{\circ}$ , be poured into cold water, a tough elastic material resembling india-rubber—called **plastic sulphur**—is obtained. Plastic sulphur is also obtained by distilling ordinary sulphur from a glass retort, and allowing the burning liquid sulphur, burning from the neck of the retort, to flow into cold water. A long continuous thread of plastic sulphur is thus obtained (Fig. 24.8).

The specific gravity of plastic sulphur is about 1.92, nearly the same as monoclinic sulphur; but unlike the crystalline varieties, this form of sulphur can be moulded between the fingers, and drawn into somewhat elastic threads. Plastic sulphur is probably a super-cooled liquid which has been hurried past its crystallizing temperature and cooled so low that it has formed a viscid mass. If cooled slowly, virtually the whole of the product is crystalline and soluble in carbon disulphide. The results of X-ray investigation of plastic sulphur show that it is mainly made up of tangled chains of sulphur atoms formed, in all probability, by the breaking open of the eight-membered rings of rhombic and monoclinic sulphur when they are melted. Plastic sulphur slowly crystallizes on standing. The change is accelerated by rubbing the mass, and is fairly rapid if the mass be heated to about  $100^{\circ}$ .

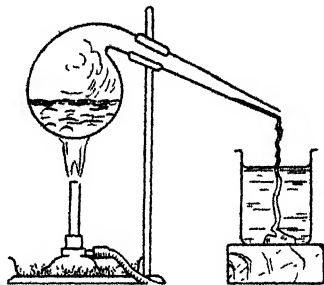


FIG. 24.8.  
Preparation of Plastic Sulphur

When this hardened substance is extracted with carbon disulphide a soluble form of sulphur (called  $S_{\lambda}$  but which may be rhombic sulphur) is obtained together with an insoluble form,  $S_{\mu}$  or amorphous sulphur.

### § 8 Amorphous Sulphur. Colloidal or $\delta$ -Sulphur

An amorphous form of sulphur known as **white sulphur** is left after extracting flowers of sulphur with carbon disulphide. A similar product is obtained by exposing a solution of sulphur in carbon disulphide to light and also by the action of water on sulphur chloride. These varieties are insoluble in carbon disulphide.

If hydrogen sulphide be passed into a saturated aqueous solution of sulphur dioxide at  $0^{\circ}$ ; or if an alcoholic solution of sulphur be poured into water; or if a saturated solution of sodium thiosulphate be mixed with twice its volume of concentrated hydrochloric acid, and cooled to  $10^{\circ}$ , **colloidal, soluble, or  $\delta$ -sulphur** is formed.

It is a clear, yellow solution containing very minute particles of sulphur in colloidal solution.

On the other hand, by acidifying sodium pentasulphide solution

sulphur is precipitated in a form soluble in carbon disulphide. This is known as **milk of sulphur**, and is almost white; on standing at ordinary temperatures, it tends to revert to rhombic sulphur, but some years may be necessary for this to be complete.

### § 9 Liquid Sulphur

Sulphur is pale yellow at ordinary temperatures, and almost colourless at  $-50^{\circ}$ , and at  $100^{\circ}$  it is intense yellow. If a piece of ordinary rhombic sulphur be gradually heated in a test-tube, the sulphur crackles and falls to pieces as indicated above. As the temperature rises, the sulphur melts to a clear, limpid, amber-coloured liquid about  $114^{\circ}$ ; the colour darkens, and the liquid loses its mobility, until, at about  $160^{\circ}$ , the mass is chestnut-coloured and so viscid that the test-tube can be turned upside down without pouring out the sulphur. The viscosity reaches a maximum at about  $180^{\circ}$  and as the temperature rises still higher, the colour becomes darker until it is almost black, but the mass becomes more and more mobile until at  $444.6^{\circ}$  the liquid begins to boil, forming a reddish-orange vapour. If the liquid be allowed to cool, the sulphur undergoes the same changes, but in the reverse order, and very slowly. If the vapour be heated to a still higher temperature, it becomes deep red at  $500^{\circ}$ , and straw-yellow at about  $650^{\circ}$ .

The dark colour of molten sulphur, as ordinarily observed, is apparently caused by the presence of traces of impurity since very carefully purified samples of sulphur are said to yield liquids which, although the viscosity changes as described, do not become darker in colour. The changes in viscosity are evidently the result of the formation of new molecular species; as mentioned above the 8-membered ring of solid sulphur is broken open and the tangled chains which result are clearly the cause of the increasing viscosity.

If  $\alpha$ -sulphur be melted at a low temperature, and the pale yellow liquid be suddenly chilled, the crystalline product is almost completely soluble in carbon disulphide; while if the dark brown liquid which is obtained when sulphur is heated to a higher temperature be similarly treated, it forms an amorphous mass almost all insoluble in carbon disulphide. It is therefore inferred that molten sulphur contains a mixture of two varieties of sulphur— $\lambda$ -sulphur and  $\mu$ -sulphur. When  $\lambda$ -sulphur solidifies it forms crystalline  $\alpha$ - or  $\beta$ -sulphur soluble in carbon disulphide; and when  $\mu$ -sulphur solidifies it forms an amorphous plastic mass insoluble in carbon disulphide. The proportion of the two varieties in any sample of sulphur can be determined by extraction with carbon disulphide, making a small allowance for the very slight solubility of the so-called "insoluble" variety. Experiment shows that there is a definite relation between the relative amounts of the two varieties present in a system in equilibrium at a definite temperature. The proportion of  $\mu$ -sulphur increases with rising temperatures, and for

each temperature there appears to be a definite equilibrium constant corresponding with the reversible reaction:  $S_\lambda \rightleftharpoons S_\mu$ . The system takes some time to attain equilibrium under any given conditions. The presence of air, sulphur dioxide, or hydrogen chloride retards, while ammonia, nitrogen, carbon dioxide, iodine, or hydrogen sulphide accelerates the speed of the change. An element exhibiting this type of behaviour is said to show **dynamic allotropy**.

### § 10 Properties of Sulphur

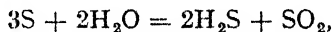
Sulphur is a yellow solid (sometimes appearing white if in a fine state of subdivision). It is tasteless and odourless, and is without physiological action on human beings, though its vapour is poisonous to lowly organized forms of life such as fungi, etc. It is a poor conductor of heat, and a non-conductor of electricity.

It is insoluble in water, sparingly soluble in alcohol and ether, and readily soluble in carbon disulphide.

Sulphur burns in air with a blue flame, and sulphur dioxide, mixed with small quantities of sulphur trioxide, is formed (see pages 487, 494). It burns very brilliantly in oxygen. When mixed intimately with substances rich in oxygen, an explosive mixture may be formed (e.g., gunpowder, page 642).

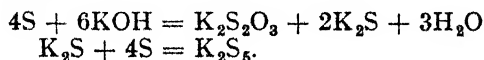
Sulphur combines directly with carbon, phosphorus, arsenic and with most metals, when the elements are heated together, the corresponding sulphides being formed. The halogens also react with sulphur, forming a variety of sulphur halides (see page 518).

Sulphur does not react with water, in the cold, but when steam is passed through boiling sulphur, a little hydrogen sulphide and sulphur dioxide are formed:



nor does it react with acids which are not able to oxidize it. It is readily oxidized by concentrated sulphuric acid or nitric acid, the products being sulphur dioxide and sulphuric acid respectively (pages 506 and 450).

It appears to dissolve in caustic alkali solutions, since it reacts with them forming sulphides and thiosulphates, e.g.,



Similar derivatives of calcium are also readily obtained (page 703).

### § 11 Uses of Sulphur

Sulphur is used in making sulphur dioxide for bleaching straw and wool; for the manufacture of sulphites for bleaching wood fibres, and removing lignin in the manufacture of wood pulp for paper-making;

and for the manufacture of sulphuric acid. It is also used in making carbon disulphide. Purified sulphur is used in making gunpowder, matches, vermilion, ultramarine, as an insulator, for vulcanizing rubber, in the manufacture of enamels and of metal-glass cements ( $S + Fe + NH_4Cl$ ). Flowers of sulphur is used as an insecticide and a fungicide, and sulphur is also employed in medicine and in industrial organic chemistry (e.g., for the production of dyes).

### § 12 Atomic Weight and Molecular Weight of Sulphur

The vapour density of very many volatile compounds of sulphur shows that these always contain, approximately, at least 32 grams of sulphur per gram-molecule, and hence that the atomic weight of sulphur is round about 32.

Exact values have been determined by several methods, e.g., by heating silver in a tube through which sulphur vapour was passed (Dumas, Stas); by reducing silver sulphide in a current of hydrogen; by converting silver sulphide into silver chloride; by converting sodium carbonate into sodium sulphate (Richards); by converting silver sulphate into the chloride by passing hydrogen chloride over it in a hot tube (Richards) and by the synthesis of silver sulphide from silver and sulphur (Hönigschmid). The accepted value at present (1957) is 32.066 based upon the work of Hönigschmid.

It is interesting to note that, since 1952, the International Table has included the following note in regard to the atomic weight of sulphur, viz., "because of natural variations in the relative abundances of the isotopes of sulphur the atomic weight of this element has a range of  $\pm 0.003$ ."

Values for the atomic weight of sulphur have also been obtained from the densities of sulphur dioxide and hydrogen sulphide.

### Molecular Weight

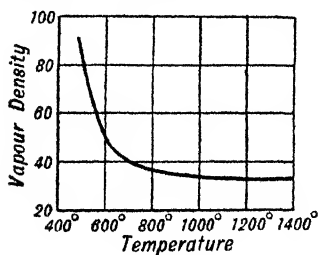


FIG 24.9.  
Vapour Density of Sulphur

At about 500° the vapour density of sulphur is nearly 96 ( $H_2 = 1$ ). This corresponds with the molecule  $S_8$ . By raising the temperature or reducing the pressure, the vapour density gradually diminishes until, at 1000°, it reaches 32, corresponding with the molecule  $S_2$ . The vapour density then remains constant up to about 1700°; at about 2000° it corresponds to a partial dissociation of 50 per cent of the  $S_2$  molecules into S atoms (see Fig. 24.9). Sulphur vapour at the

temperature at which it boils under a pressure of 2 mm. (i.e., 193°) has a density corresponding to a molecule  $S_8$ .



It may be that at temperatures intermediate between  $1000^{\circ}$  and  $500^{\circ}$ , some or all of the molecules  $S_8$ ,  $S_6$ ,  $S_4$ , and  $S_2$  are present, but the curve is steadily depressed with rising temperatures, and it shows no signs of flattening such as might be expected if any particular type of molecule predominated throughout any particular range of temperature. The freezing and boiling-point methods for the determination of molecular weights show that the molecule of sulphur in solution in carbon disulphide or bromoform exists as  $S_8$ , a result in harmony with the conclusions from X-ray data (*v.* page 476).

### § 13 Hydrogen Sulphide or Sulphuretted Hydrogen, $H_2S$

#### History and Occurrence

##### Historical

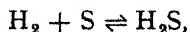
Several references to hydrogen sulphide appear in the writings of the alchemists of the Middle Ages, where it is described under the general term "sulphurous vapour," and their directions for the preparation of this product show that they referred to some fetid solutions of the polysulphides which probably contained this gas. This liquid excited the attention of the alchemists, for it gave all kinds of colorations with solutions of the different metals; with vinegar, it gave a precipitate of sulphur and at the same time gave off a gas which blackened silver and some other metals. K. W. Scheele (1777) was the first to investigate the compound systematically.

##### Occurrence

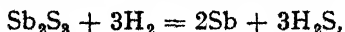
Hydrogen sulphide occurs in several mineral waters, in the exhalations from volcanic vents, etc. It is also formed during the putrefaction of animal and vegetable matters containing sulphur, and by the action of an aqueous solution of carbonic acid on sulphides which in turn are often formed by the reduction of sulphates by organic matter. Several bacteria during the putrefaction of organic matter produce hydrogen sulphide—the sulphur being derived from protein matters and from the reduction of sulphates—stimulated possibly by sunlight. This is said to occur at the mouths of rivers on the West Coast of Africa—e.g., the Congo river, which brings organic matter into intimate contact with sulphides. Hence, the atmosphere may be contaminated by hydrogen sulphide derived from these three causes. Hydrogen sulphide is readily oxidized and it cannot therefore persist very long in the atmosphere.

### § 14 Preparation of Hydrogen Sulphide

Hydrogen sulphide is formed in small quantities when a stream of hydrogen is passed through boiling sulphur:

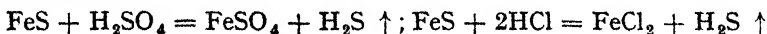


but the method is not of practical importance. It is also formed when hydrogen is passed over certain heated sulphides, e.g.:



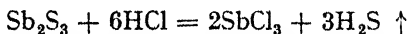
and by the action of sulphur upon organic matter when warmed.

The gas is best prepared by the action of dilute hydrochloric or sulphuric acid upon ferrous sulphide,  $\text{FeS}$ , which, in turn, is made by heating iron and sulphur together (page 921). The reactions are symbolized:



Hydrochloric acid is generally preferred to sulphuric acid because the resulting ferrous chloride— $\text{FeCl}_2$ —is not so liable to crystallize out as ferrous sulphate— $\text{FeSO}_4$ . For small quantities, a similar apparatus to that employed for the preparation of carbon dioxide (Fig. 22.14) may be used; and for larger quantities, Kipp's apparatus may be used (Fig. 20.2). Comparatively large quantities of the gas are required intermittently in a testing laboratory, and Kipp's apparatus is commonly used for the purpose. The gas is generally washed by passing it through a wash-bottle containing water.

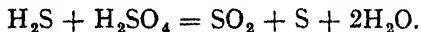
Artificial ferrous sulphide, prepared as indicated above, generally contains a little free iron, and hence some hydrogen will be mixed with the gas. For ordinary purposes, this does not matter. The gas may also contain traces of hydrocarbons, etc., derived from the action of the acids on the impurities in the iron. A purer gas is made by heating antimony sulphide with concentrated hydrochloric acid, and washing the gas in water:



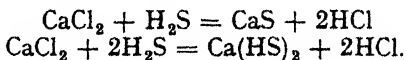
Aluminium sulphide with water also gives hydrogen sulphide.

Very pure hydrogen sulphide is best obtained by solidifying the crude gas with liquid air. The main impurity is hydrogen, which is not condensed under these conditions and so can be pumped off. The residual solid is allowed to warm up slowly, and after the first portions have been allowed to escape, pure hydrogen sulphide is obtained.

Hydrogen sulphide is rather soluble in cold water and so cannot be collected over it, but it can be collected over warm water. It can be dried by means of dehydrated alumina or phosphorus pentoxide, but sulphuric acid must not be used because it is reduced:



Calcium chloride is often used for drying the gas in spite of the fact that slight decomposition occurs:



### § 15 Properties of Hydrogen Sulphide

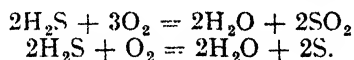
Hydrogen sulphide is a colourless gas with an unpleasant smell like rotten eggs. It has a sickly taste resembling its smell. It is very poisonous, a proportion of 1 part in 1000 in air proving fatal, if breathed for any length of time. Very dilute chlorine is recommended as an antidote.

Hydrogen sulphide was liquefied by Faraday in 1823. It condenses to a colourless liquid at  $10^{\circ}$  under a pressure of 15 atmospheres. At ordinary pressures the liquid boils at  $-61.8^{\circ}$  and freezes at  $-82.9^{\circ}$ .

Hydrogen sulphide is slightly denser than air and is fairly soluble in cold water, which dissolves 4.62 times its volume at  $0^{\circ}$  and 2.55 volumes at  $20^{\circ}$ . The solution is called "hydrogen sulphide water" and has a slightly acid reaction. The solution decomposes slowly, depositing sulphur—particularly if exposed to light:



Hydrogen sulphide burns in air with a bluish flame forming sulphur dioxide and water if excess of air be present; or sulphur and water when there is insufficient air for complete combustion. Sulphur is thus deposited on a cold object placed in the flame:



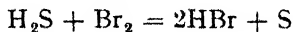
A mixture of two volumes of hydrogen sulphide with three volumes of oxygen explodes violently when ignited. A lighted taper dipped into a jar of the gas is extinguished showing that it is a non-supporter of combustion.

Hydrogen sulphide is easily dissociated by passing it through a hot porcelain tube.



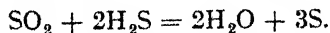
The dissociation begins at about  $400^{\circ}$ , and it is complete at about  $1700^{\circ}$ . It will be remembered that hydrogen sulphide may be formed by passing hydrogen through boiling sulphur. This means that the reaction belongs to the type of reversible reactions—discussed on page 241. Hydrogen sulphide is also decomposed by passing electric sparks through the gas confined in a tube over mercury.

Hydrogen sulphide behaves as a reducing agent. Thus it reduces the halogens to halogen acid, e.g.



(a reaction made use of for the preparation of hydrobromic and hydriodic acids, pages 560, 568), ferric salts to ferrous salts, dichromates to chromic salts, permanganates to manganous salts, sulphuric acid to

sulphur dioxide, etc. Its reaction with sulphur dioxide may be noticed, taking place readily when jars of the moist gases are mixed:

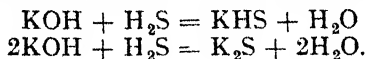


If the gases be well dried no reaction occurs (cf. page 317).

Hydrogen sulphide behaves in some reactions as a weak acid, e.g., with heated metals, when the sulphide and hydrogen are formed:



or with alkalis, when hydrosulphides and sulphides are formed:



### § 16 The Action of Hydrogen Sulphide on Metallic Salt Solutions

Hydrogen sulphide is an important reagent in qualitative analysis since its reactions with the different metallic salts enable the metals to be separated into groups as a preliminary to more detailed examination. Thus:

I. Sulphides insoluble in dilute acids.

(a) Soluble in alkaline sulphides—arsenic, antimony, stannic, molybdenum, and tungsten sulphides.

(b) Insoluble in alkaline sulphides—mercury, silver, lead, copper, bismuth, cadmium, and stannous sulphides.\*

II. Sulphides precipitated by ammonium sulphide but soluble in dilute mineral acids—iron, cobalt, nickel, manganese, and zinc sulphides.

III. Sulphides not precipitated by hydrogen sulphide or by ammonium sulphide—chromium, aluminium, magnesium, barium, strontium, calcium, potassium, and sodium. Chromium and aluminium are precipitated as hydroxides.

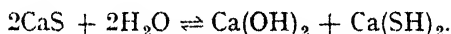
The method of classifying certain elements into groups—those which form soluble and those which form insoluble sulphides in hydrochloric acid—frequently conveys wrong ideas of the properties of the sulphides. The solubility of the sulphides depends upon the concentration of the acid. For instance, if hydrogen sulphide be passed into 5 ml. of a solution of 2 grams of tartar emetic—potassium antimonyl tartrate—in 15 ml. of hydrochloric acid (sp. gr. 1.175) and 85 ml. of water, antimony sulphide will be precipitated, but not if 15 ml. of hydrochloric acid had been employed without the water.

Under ordinary conditions, the solubilities of the sulphides in hydrochloric acid, starting with the least soluble, are approximately in the order:

As, Hg, Cu, Sb, Bi, Sn(ic), Cd, Pb, Sn(ous), Zn, Fe, Ni, Co, Mn.

\* Stannous sulphide is soluble in *yellow* ammonium sulphide.

Elements wide apart in the list can be easily separated by hydrogen sulphide in acid solutions, but elements close together in the list require a very careful adjustment of the amount of acid in solution before satisfactory separations can be made. For instance, the separation of cadmium or lead from zinc by means of hydrogen sulphide is only satisfactory when the concentration of the acid is very carefully adjusted. If too much acid be present, cadmium or lead will be imperfectly precipitated; while if too little acid be present, zinc will be precipitated with the cadmium or lead. Hence there is no sharp line of demarcation between metals precipitated and metals not precipitated by hydrogen sulphide from acid solutions. All depends upon the concentration of the acid. This is adjusted so that antimony, arsenic, lead, bismuth, cadmium, copper, mercury, and tin are precipitated while the aluminium, iron, zinc, nickel, cobalt, and manganese salts will be found in the filtrate. Barium, strontium, calcium, and magnesium salts will also be found in the filtrate along with the alkalis, because the sulphides of these elements are attacked and decomposed by water and by acids. E.g.:



These facts may be explained by the application of the electrolytic dissociation theory. (Cf. pages 263-66.)

### § 17 Formula of Hydrogen Sulphide

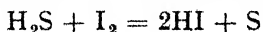
If a known volume of hydrogen sulphide be heated with metallic tin in a tube over mercury, tin sulphide and free hydrogen equal to the original volume of hydrogen sulphide are formed; similarly, hydrogen sulphide, when decomposed by electric sparks, suffers no change in volume. That is to say, hydrogen sulphide contains its own volume of hydrogen and hence, from Avogadro's hypothesis, it follows at once that one molecule of hydrogen sulphide contains one molecule—two atoms—of hydrogen, and that the formula of hydrogen sulphide is  $\text{H}_2\text{S}_n$ , where  $n$  has also to be determined.

Its vapour density is 17, hence its molecular weight is 34 and molecular formula  $\text{H}_2\text{S}$ .

### § 18 Detection and Determination of Hydrogen Sulphide

Hydrogen sulphide is very easily detected by its action on solutions of soluble lead salts. Papers soaked in lead acetate solution turn first brown and then black on exposure to the gas, owing to the formation of lead sulphide.

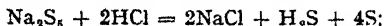
It is determined by treatment with excess of a standard solution of iodine in potassium iodide (page 567), making use of the reaction:



and then, after a short period, determining the excess iodine by titration with sodium thiosulphate solution.

### § 19 Hydrogen Persulphide or Hydrogen Disulphide

If dilute hydrochloric acid be poured into a solution of sodium polysulphide, e.g.,  $\text{Na}_2\text{S}_6$ , milk of sulphur is precipitated (page 477):



but if the polysulphide be poured into the acid, little or no hydrogen sulphide is evolved, and a yellow oil separates.

This was once considered to be a mixture of **hydrogen pentasulphide**,  $\text{H}_2\text{S}_5$ , with other hydrogen polysulphides. When the oil is distilled under reduced pressure, the fraction which is obtained at  $69^\circ$  under a pressure of 2 mm. of mercury is a pale yellow oil with a molecular weight, by the freezing-point method, corresponding with  $\text{H}_2\text{S}_3$ —**hydrogen trisulphide**. The fraction which distils at  $74^\circ$ – $75^\circ$ , under atmospheric pressure, has the composition  $\text{H}_2\text{S}_2$ . This is hydrogen disulphide or hydrogen persulphide. The persulphide dissolves in benzene, forming a clear solution. Hydrogen persulphide is a colourless oily liquid with a specific gravity 1.376. It has a pungent irritating smell, and decomposes gradually into hydrogen sulphide and sulphur. The decomposition is faster in presence of water, and particularly alkalis. Mere contact with glass, paper, dust, etc., induces rapid decomposition. Hydrogen persulphide burns with a blue flame. Like its analogue, hydrogen peroxide, it has oxidizing and reducing qualities. Its structure has been shown to be  $\text{H}-\text{S}-\text{S}-\text{H}$ .

Hydrogen trisulphide,  $\text{H}_2\text{S}_3$ , prepared as just described, resembles the persulphide in many of its properties, but its specific gravity is 1.496, and it solidifies between  $-52^\circ$  and  $-54^\circ$ . Nothing is known about the structure of hydrogen trisulphide.

The three hydrogen sulphides— $\text{H}_2\text{S}$ ,  $\text{H}_2\text{S}_2$ , and  $\text{H}_2\text{S}_3$ —are all the hydrogen polysulphides whose individuality has been clearly demonstrated, although a whole series ranging from  $\text{H}_2\text{S}_4$  to  $\text{H}_2\text{S}_9$  has been reported.

### § 20 Sulphur Dioxide, Sulphurous Anhydride, $\text{SO}_2$

#### History and Occurrence

The use of sulphur for disinfecting purposes has been known from very early times. It is referred to in Homer where Odysseus, after the slaughter of the suitors, and probably recognizing the need for a general cleansing, calls:

Quickly, O Nurse, bring fire that I may burn  
Sulphur, the cure of ills.

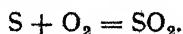
J. Priestley (1770) prepared the gas by the action of hot concentrated sulphuric acid on mercury. Priestley called it sulphurous acid.

Sulphur dioxide is found among the fumes from volcanic vents; in the springs of volcanic districts, and in the air of towns where it is derived from the sulphur compounds in coal.

It is also found in the effluent gases from many industrial operations, e.g., the roasting of zinc blende in the smelting of zinc (page 715). The sulphur dioxide contained in such gases is being increasingly used for the manufacture of sulphuric acid, etc. (page 497).

### Preparation

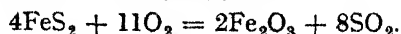
Sulphur dioxide is formed when sulphur is burned in air:



Between 6 and 8 per cent of the sulphur is simultaneously oxidized to sulphur trioxide,  $\text{SO}_3$ . If the sulphur be burnt in oxygen gas between 2 and 3 per cent burns to sulphur trioxide.\* The nitrogen in the air seems to favour the production of sulphur trioxide, whereas moisture and carbon dioxide do not affect the result appreciably. The proportion of sulphur trioxide formed increases with the pressure. When sulphur is oxidized by a higher oxide—e.g., manganese dioxide—sulphur dioxide is formed:



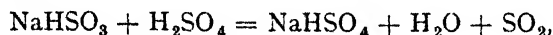
Sulphur dioxide is also formed when the sulphides of some metals are roasted in air—e.g., iron or copper pyrites:



This reaction is very commonly used for making the sulphur dioxide employed in the manufacture of sulphuric acid.

Prepared in this way from iron pyrites, the gas frequently contains arsenic, the presence of which, for many purposes, is highly injurious, and so it has to be removed.

In the laboratory a supply of the gas is often obtained from a siphon of the liquid (cf. page 489) but it can be prepared also either by the action of moderately concentrated sulphuric acid on sodium sulphite or bisulphite, e.g.,



or by heating concentrated sulphuric acid with a suitable reducing agent such as copper, mercury, sulphur, etc. Copper is frequently used for this purpose.

The process is illustrated in Fig. 24.10. The flask is about one-third filled with copper turnings and sufficient concentrated sulphuric acid is added not quite to cover the copper. On heating, sulphur dioxide is evolved, and may be passed through wash-bottles containing concentrated sulphuric acid to dry it. It is collected by downward delivery as shown since it is soluble in water.

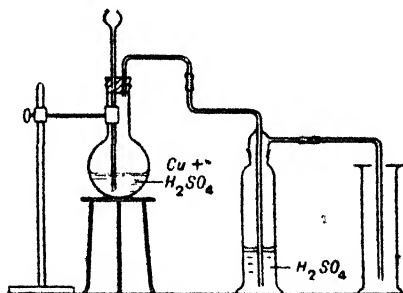


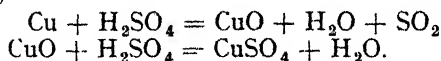
FIG 24 10  
Preparation of Sulphur Dioxide

\* The presence of sulphur trioxide in the sulphur dioxide formed when sulphur burns in air accounts for the "foggy" appearance of the gas. This will be understood when the properties of the trioxide have been studied.

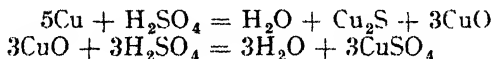
The reaction is commonly represented by the equation:



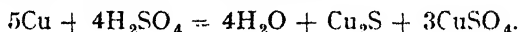
but it is certainly more complex than this. It is probable that the first action is the oxidation of the copper, with consequent reduction of the sulphuric acid to sulphur dioxide. The copper oxide then reacts with more sulphuric acid, forming the salt—copper sulphate—in the usual way.



In addition to this degree of complexity, some side reaction occurs which results in the formation of cuprous sulphide, which causes the residue in the flask after the experiment to appear black. This may be formed by some such series of reactions as:



which, summarized, leads to the equation:



Industrially, sulphur dioxide is prepared by roasting iron pyrites, from waste gases of metallurgical operations and by burning sulphur in air.

In Germany, sulphur dioxide for liquefaction (for which purpose the very dilute gas from the other methods mentioned is not very suitable) has been made by reducing the trioxide with sulphur. Oleum (page 503), containing 22 per cent of  $\text{SO}_3$ , was used as the source of sulphur trioxide and was heated with sulphur at  $110^\circ$ .

Anhydrite (a form of calcium sulphate) is now being used increasingly as a source of sulphur dioxide for the manufacture of sulphuric acid (cf. page 503).

## § 21 Properties of Sulphur Dioxide

Sulphur dioxide is a colourless gas with a smell characteristic of burning sulphur. Sulphur dioxide is an acute blood poison. Sulphur dioxide is also injurious to vegetation, and it is one of the "noxious vapours" complained about in manufacturing districts.

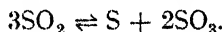
The gas is more than twice as dense as air, and in consequence it can be collected by downward delivery. It cannot be collected satisfactorily over water because it is easily soluble. One volume of water at  $0^\circ$  dissolves 79.8 volumes of sulphur dioxide; and at  $20^\circ$ , 39.4 volumes. The aqueous solution is strongly acid, and it has the general properties characteristic of acids.

The gas is easily liquefied. A pressure of 1.5 atmospheres suffices for the condensation of the gas at  $0^\circ$ ; and at  $-10^\circ$  the gas liquefies



under ordinary pressures. In order to liquefy it, it is therefore sufficient to dry thoroughly the gas obtained by the action of copper on sulphuric acid, and then lead the gas through a condensing tube immersed in a freezing mixture. The gas condenses to a clear, colourless, transparent, limpid liquid which boils at  $-10^{\circ}$  and solidifies at  $-72.7^{\circ}$  to a white snow-like mass. Liquid sulphur dioxide is sold commercially in thick glass "siphons," and where available, the "siphons" are used as a source of sulphur dioxide for laboratory work. By the evaporation of liquid sulphur dioxide a temperature approaching  $-50^{\circ}$  can be obtained. Hence like ammonia and carbon dioxide, sulphur dioxide is used as a refrigerating agent. Liquid sulphur dioxide is a good solvent for phosphorus, iodine, sulphur, resins, etc. It will also dissolve a number of salts and the conductivity of these solutions is sometimes greater than that of aqueous solutions. This is because its dielectric constant is fairly high although it is not so high as that of water.

Sulphur dioxide is decomposed at high temperatures; for example, by passage of electric sparks. It is appreciably dissociated at  $1200^{\circ}$ , sulphur trioxide (or, if moist, sulphuric acid) and sulphur being formed:



It is also decomposed by light, for if a beam of light be sent through a long cylinder of the gas, at first the gas appears to be clear and transparent, but in a few minutes the gas appears to decompose, for misty wavering striae appear, and gradually the whole tube appears to be filled with a fog, due to the decomposition of the sulphur dioxide. If left a short time in the dark, the gas becomes clear owing to the recombination of the sulphur and sulphur trioxide, or to condensation of the solid products on the walls of the apparatus.

Electrical discharge at low pressures appears to convert sulphur dioxide into sulphur monoxide (page 513).

Sulphur dioxide combines reversibly with oxygen when heated, sulphur trioxide being formed (page 494):



The reaction is only slow in the absence of a catalyst; the most efficient catalyst is platinum (see below, page 494).

Sulphur dioxide reacts with chlorine and fluorine, combining directly to form sulphuryl chloride,  $\text{SO}_2\text{Cl}_2$ , and sulphuryl fluoride, respectively. The reaction between sulphur dioxide and chlorine is catalysed by the presence of camphor (page 517).

Sulphur dioxide is incombustible and a non-supporter of ordinary combustion. Some substances are able to burn in the gas by abstracting its oxygen. Ignited magnesium ribbon, for instance, continues to burn in the sulphur dioxide. Potassium, calcium, tin, lead, iron, arsenic, and antimony also burn when the finely divided element is heated in an atmosphere of sulphur dioxide. The products of the reaction are

R\*

oxides, sulphides, and occasionally free sulphur. Sulphur dioxide is decomposed by carbon at  $1100^{\circ}$  (cf. page 473):



Sulphur is deposited when hydrogen sulphide and sulphur dioxide are brought into contact, say, by placing a jar of sulphur dioxide and of hydrogen sulphide mouth to mouth. The gaseous exhalations from some volcanoes contain these two gases which, on mingling together, mutually decompose with the formation of sulphur (page 484). This reaction does not occur if the gases are thoroughly dried.

Sulphur dioxide in the presence of moisture is a well-known reducing agent. (See under sulphurous acid—below.)

## § 22 Uses of Sulphur Dioxide

Sulphur dioxide is used in the manufacture of sulphuric acid, as a refrigerating agent, as a solvent for extracting glue, gelatine, etc., for preserving meats, wines, etc. It prevents the growth of certain moulds and kills certain disease germs; hence its use for fumigation (see below). It is used in sugar manufacture, as a bleaching agent for straw, silk, wool, and goods too delicate for treatment with chlorine.

On account of its poisonous nature, it was formerly extensively used for fumigation purposes (e.g., in the form of sulphur candles), but its use for this purpose has of late years been discontinued in favour of formaldehyde.

Very large quantities are used in the preparation of calcium hydrogen sulphite for the manufacture of paper from wood pulp.

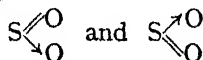
Its properties as a solvent have been made use of in the petroleum industry.

## § 23 Formula of Sulphur Dioxide

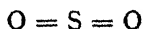
When sulphur burns in oxygen no change in volume occurs. The apparatus shown in Fig. 22.14 (page 391) can be used to show this.

A small piece of sulphur in a metal spoon is ignited in *dry* oxygen over *dry* mercury by means of a platinum wire which can be heated electrically. The result shows that sulphur dioxide contains its own volume of oxygen, and hence that the formula is  $\text{S}_n\text{O}_2$ , where  $n$  is still to be determined. The vapour density is found to be close to 32 ( $\text{H}_2 = 1$ ) and hence  $n = 1$  and the molecular formula is  $\text{SO}_2$ .

The constitution of sulphur dioxide is now thought to be a resonance hybrid between the forms



It cannot be



as the molecule is not linear.

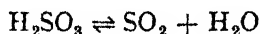
### § 24 Sulphurous Acid, $\text{H}_2\text{SO}_3$

As mentioned above, the aqueous solution of sulphur dioxide is markedly acidic and is believed to contain **sulphurous acid**,  $\text{H}_2\text{SO}_3$ . This acid cannot be isolated, but its presence is inferred from the following facts:

(i) the solution of sulphur dioxide does not obey Henry's Law (page 189), even approximately;

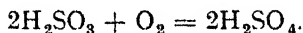
(ii) the solution behaves in many ways like an acid; witness its effect on indicators, and formation of salts (sulphites) with metals and basic oxides. It is also an electrolyte, that is, it conducts electricity.

The solution smells strongly of sulphur dioxide, and the gas is expelled completely on boiling, hence it is probable that free sulphur dioxide is present in equilibrium with the sulphurous acid:



(cf. carbonic acid, page 393).

Moist sulphur dioxide and solutions of the gas are powerful reducing agents owing to the ease with which sulphurous acid is oxidized to sulphuric acid:

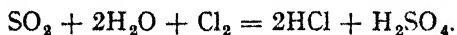


It reduces permanganates to manganous salts; chromates to chromic salts; ferric to ferrous salts, etc. The last reaction is often used in analytical work for the reduction of iron previous to its determination by volumetric processes.

The bleaching effects of sulphurous acid result from its reducing properties. Moistened red rose-leaves, or fabrics dyed with, say, "magenta" dye, when placed in the gas lose their colour. The sulphur dioxide appears to react with the colouring matter, forming sulphuric acid and hydrogen, and the nascent hydrogen bleaches by reducing the colouring agent. This idea is supported by the fact that the colour of many articles bleached by sulphur dioxide can be restored by exposing the article to oxidizing conditions.

Dry sulphur dioxide, like dry chlorine, does not bleach.

An aqueous solution of sulphur dioxide reduces chlorine, forming hydrochloric and sulphuric acids:

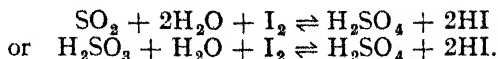


Hence sulphurous acid is used as an "anti-chlor," that is, as an agent to remove the last traces of chlorine from articles bleached with chlorine.

Sulphur dioxide reduces iodine to hydrogen iodide in the presence of water.

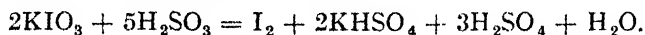
On the other hand, concentrated solutions of hydrogen iodide are

oxidized by sulphurous acid with liberation of iodine. The reaction is, in fact, a reversible one:



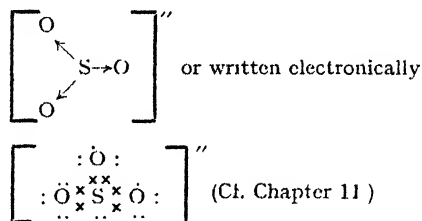
This reaction is important because the amount of sulphurous acid or of its salts in a given solution can be determined by adding a solution of iodine of known strength from a burette until the iodine solution is no longer decolorized. The amount of sulphur dioxide must not exceed 0.05 per cent or the "back reaction" will appreciably affect the results.

Iodates are reduced to iodine by sulphurous acid, a reaction which can be used for the detection of sulphur dioxide:

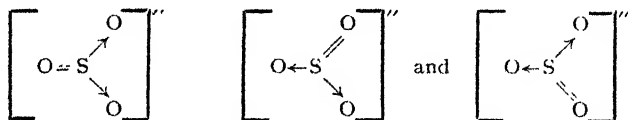


This reaction is applied in the extraction of iodine from the sodium iodate present in Chile saltpetre (page 565).

The constitution of sulphurous acid is a matter about which there has been much controversy. X-ray analysis and electron diffraction experiments have shown that the sulphite ion is probably in the form of a pyramid with the sulphur atom at one apex and the oxygen atoms at the others. The ion may then be

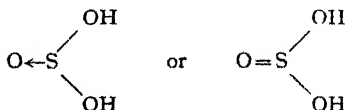


The most recent work has, however, suggested that the ion exhibits a considerable amount of double-bond character, if so it is probable that it is a resonance hybrid of the forms:

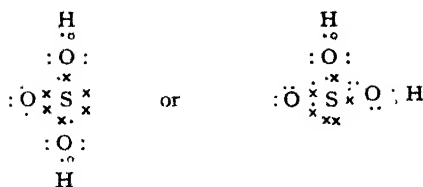


The structure of sulphurous acid itself is still in doubt.

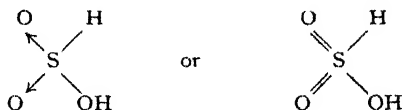
Thionyl chloride  $\text{Cl} \cdot \text{SO} \cdot \text{Cl}$  (page 516) yields diethyl sulphite,  $\text{C}_2\text{H}_5\text{O} \cdot \text{SO} \cdot \text{OC}_2\text{H}_5$ , when treated with alcohol, while sodium sulphite and ethyl iodide give ethyl sulphonic acid,  $\text{C}_2\text{H}_5\text{SO}_2\text{OH}$ . This evidence suggests that sulphurous acid may exist in two forms, one having an unsymmetrical and the other a symmetrical structure. Both these structures can be formulated in two ways, thus the symmetrical form may be



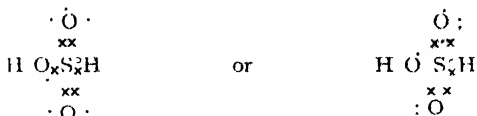
ie



and the unsymmetrical



or, written electronically,



## § 25 Sulphites

The salts of sulphurous acid are known as sulphites, and two series of these are known, viz., normal sulphites, and acid sulphites or bisulphites, thus indicating that the acid is a dibasic acid. The sulphites of the alkali metals and of the alkaline earths are described later under the heading of the metal concerned.

The normal sulphites are stable, and their solutions do not smell of sulphur dioxide. They decompose with acids forming first, presumably, sulphurous acid, which breaks down into sulphur dioxide (which is evolved as a gas) and water. Sulphites can be distinguished from sulphates since although they give a white precipitate (of barium sulphite) with barium chloride solution, this precipitate is soluble in dilute hydrochloric acid, whereas barium sulphate is not. Sulphites are recognized by the evolution of sulphur dioxide in the cold, on the addition of dilute hydrochloric acid. The sulphur dioxide is identified by its action on filter paper soaked in potassium chromate or dichromate solution. A green colour indicates the presence of sulphur dioxide. Sulphites are distinguished from thiosulphates (page 512) since these give a precipitate of sulphur as well as sulphur dioxide with dilute acids. The sulphites are reducing agents, like sulphurous acid, being readily convertible into sulphates.

Bisulphites are not known in the solid state. If a solution of a bisulphite be evaporated sulphur dioxide is evolved and the normal sulphite is obtained; if the evaporation be carried out in an atmosphere of sulphur dioxide the *metabisulphite* (e.g.,  $\text{Na}_2\text{S}_2\text{O}_5$ ) results.

*Sodium metabisulphite* (sometimes known as the *disulphite* or *pyrosulphite*) is prepared by saturating a hot saturated aqueous solution of sodium carbonate with sulphur dioxide and allowing the solution to cool. It is used in photography for the preparation of acid fixing baths, in the tanning industry as a reducing agent for "chrome" solutions, as an "antichlor," a food and silage preservative, and in the production of crepe rubber.

## § 26 Sulphur Trioxide, Sulphuric Anhydride, $\text{SO}_3$

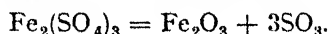
### History

Sulphur trioxide seems to have been made by "B. Valentine" in the seventeenth century, and called "philosophical salt." K. W. Scheele (1777) and G. de Morveau (1786) called it the anhydride of sulphuric acid.

### Preparation

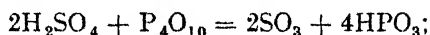
Sulphur trioxide can be obtained

(i) by the dry distillation of ferric sulphate:

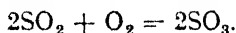


Some other sulphates behave similarly;

(ii) by the action of excess of phosphorus pentoxide on concentrated sulphuric acid, when the acid is dehydrated:



(iii) by the direct union of sulphur dioxide and oxygen:



This is now the only important method of making sulphur trioxide.

This last reaction is discussed in some detail on page 501 in connection with the manufacture of sulphuric acid by the contact process (page 502). A catalyst is necessary; the most efficient catalyst is platinum in presence of which the reaction proceeds quickly and almost to completion at  $400^\circ$ . Industrially, vanadium pentoxide has now largely replaced platinum for this purpose.

Sulphur trioxide may be prepared in this way in the laboratory using the apparatus sketched in Fig. 24.11.

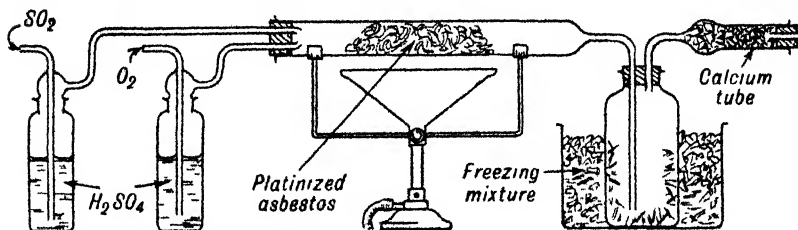


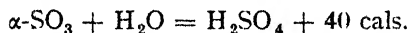
FIG. 24 11.--Preparation of Sulphur Trioxide

Sulphur dioxide from a siphon and oxygen are dried by passing through wash-bottles containing concentrated sulphuric acid and then mixed at the entrance to a hard glass tube containing platinized asbestos (page 943) which is heated to a temperature of about 400°. Sulphur trioxide is formed in white clouds which condense, in a freezing mixture, if the apparatus is absolutely dry, in the form of silky needles.

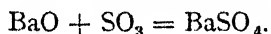
### § 27 Properties of Sulphur Trioxide

Sulphur trioxide exists in several forms. The vapour, on cooling, first condenses to a liquid form, of boiling point 44·8°; this on standing for a short time solidifies to transparent crystals which melt at 16·85°, boil at 44·52° and have a specific gravity of 1·9225. This is known as the "ice" form or  $\alpha$ -sulphur trioxide. On standing for a longer period at room temperature the  $\alpha$ -form passes gradually in mass of silky crystals resembling asbestos. This form is therefore known as the "asbestos" form or  $\beta$ -sulphur trioxide. At 50° this form slowly changes into the  $\alpha$ -form. It melts at 32·5°. A third jelly-like solid form, known as the  $\gamma$ -form, has also been reported. Of these solid forms the  $\beta$ -form is believed to be the most stable at ordinary temperature but all three solid forms appear to be able to exist together in metastable equilibrium since the change from one form to another is very slow especially if water (and hence sulphuric acid) is completely absent.

The forms are not very different chemically although the  $\beta$ -sulphur trioxide reacts somewhat less vigorously than the  $\alpha$ -variety. Both dissolve in water with a hissing sound as if a piece of red-hot iron were being plunged into the water; much heat is evolved, and sulphuric acid is produced:

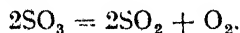


Hence sulphur trioxide is also called **sulphuric anhydride**. The anhydride does not redden blue litmus if extreme precautions be taken to exclude moisture. Sulphur trioxide reacts directly with many metallic oxides, forming the corresponding **sulphates**, e.g., with barium oxide:



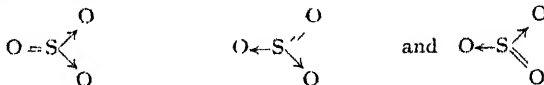
So much heat is evolved that the mass becomes incandescent. Sulphur trioxide also forms curious addition products with some elements, e.g.,  $\text{I}_2(\text{SO}_3)_6$ ,  $\text{Te}(\text{SO}_3)_4$ .

When heated to 1000°, sulphur trioxide decomposes completely into sulphur dioxide and oxygen:



Two volumes of sulphur trioxide produce two volumes of sulphur dioxide and one volume of oxygen. This corresponds with the formula  $(\text{SO}_3)_n$ . The molecular weight of the  $\alpha$ -form, indicated above, shows that its formula must be  $\text{SO}_3$ ; and the  $\beta$ -form,  $\text{S}_2\text{O}_6$ .

The structure of the sulphur trioxide molecule is now believed to be a resonance hybrid of the structures



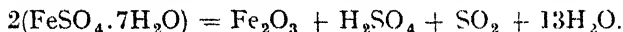
The molecule is planar

## § 28 Sulphuric Acid, $\text{H}_2\text{SO}_4$

### History and Occurrence

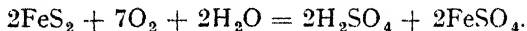
Sulphuric acid does not seem to have been known to the ancient world, and the earliest mention of it is probably in the Latin version of Geber. If the work ascribed in these writings to Geber is really his, sulphuric acid must have been known by the ninth century; but it is very doubtful if this is so, and hence the discovery of sulphuric acid is more probably to be assigned to the thirteenth century.

It was commonly made in the later middle ages by distilling ferrous sulphate crystals, from which it derives its name *oil of vitriol*.



For a long time it was made by burning a mixture of sulphur and nitre over water, this process being the forerunner of the lead chamber process for its manufacture (see below).

Free sulphuric acid is sometimes found in mineral springs whose waters have been in contact with sulphide minerals such as iron pyrites:



The waters of the Rio Tinto river in Spain contain considerable quantities of sulphuric acid on this account.

## § 29 The Manufacture of Sulphuric Acid

The manufacture of sulphuric acid is a world industry of vast importance, the production in the year 1952 being about twenty-three million tons. Of this total that acid which is required to be of moderate concentration only is mainly made by the lead chamber process; acid of high concentration (98 per cent or higher (including oleum, page 503)) is made by the contact process.

### The Lead Chamber Process

The first beginnings of this process, on a manufacturing scale, were made by Ward who, in 1740, prepared sulphuric acid by burning sulphur with nitre in large glass vessels—40 to 60 gallons capacity—time after time, until the acid which collected on the bottom of the vessels was strong enough to pay for its concentration in glass retorts.



The acid was sold as "oil of vitriol made by the bell," to distinguish it from the acid made from ferrous sulphate. Roebuck and Garbett substituted lead chambers for Ward's glass vessels in a works at Birmingham in 1746. F. Clément and J. B. Désormes, in 1793, showed that the process could be made continuous, and that the nitre plays an intermediary part between the sulphur dioxide and the air.

Fig. 24.12 is a diagram of the modern plant.

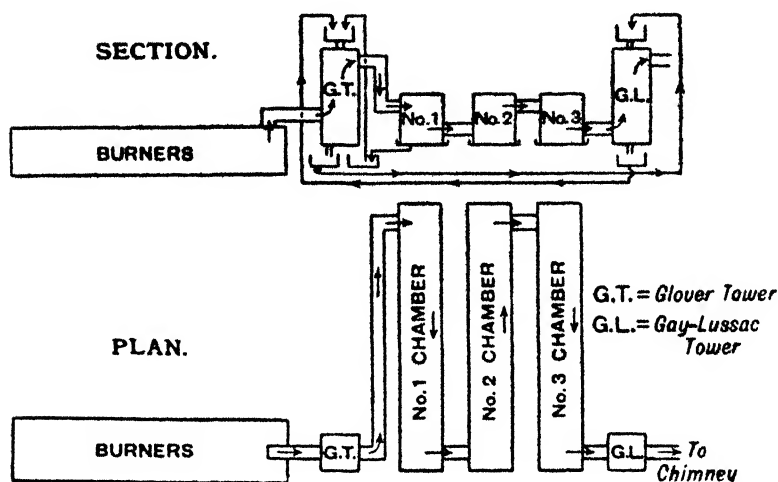
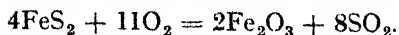


FIG 24 12 — Chamber Process for Sulphuric Acid Manufacture

Sulphur dioxide is made in the burners, very often from iron pyrites, but other sources such as native sulphur, spent oxide from gasworks (page 382) and the flue gases produced in smelting ores such as those of zinc and copper may be used instead. The last-named source of sulphur for sulphuric acid manufacture has recently become much more important, since it is now possible to reduce sulphur dioxide to sulphur on a manufacturing scale, and so obviate the transport difficulty (see page 473).

The type of burner used varies with the material being burnt. If iron pyrites in lumps be the source of sulphur no special arrangements are necessary, but more finely divided materials require the use of special furnaces, fitted with mechanically operated stirrers which constantly expose fresh surfaces of the burning material to the air. The air supply is so adjusted that excess of oxygen is present in the gases which leave the burners, ready for the next stage of the process:



Oxides of nitrogen made by the oxidation of ammonia (cf. page 448) are then mixed with the gases which are then freed from dust and then

passed into the base of the Glover tower. This is a tower, lined with acid-proof material, packed with flints, down which trickles a mixture of a weak acid from the lead chambers and the strong nitrated acid which has been used to absorb nitrous fumes, and recovered in the Gay-Lussac tower to be described later. The functions of the Glover tower are: (1) to recover the nitrogen oxides from the Gay-Lussac tower; (2) to cool the gases from the burners; (3) to help to concentrate the acid trickling down the tower; and (4) partly to oxidize the sulphur dioxide from the burners.

The mixture of air, sulphur dioxide, and nitrous fumes passes into a set of three leaden chambers, which may be of a total capacity of 150,000 cubic feet, into the top of which a fine spray of water is blown. The gases in the chambers are thus intimately mixed. The oxidation of the sulphur dioxide mainly occurs in the first two chambers. The gases are passed through the chambers slowly so as to allow time for all the sulphur dioxide to be oxidized. The third chamber serves mainly to dry the gases. The chambers are kept cool enough to condense the sulphuric acid which collects on the floor from which it is run off, a constant level being maintained in the chambers. It is called *chamber acid*. Chamber acid contains between 62 and 70 per cent  $\text{H}_2\text{SO}_4$ .

The excess air which leaves the lead chambers is highly charged with nitrogen oxides. These are recovered by causing the exit gases from the chambers to pass up a tower called the Gay-Lussac tower, packed with coke, down which concentrated sulphuric acid is trickling. The concentrated acid absorbs the nitrous fumes. The "nitrated acid" which collects at the foot of the Gay-Lussac tower is pumped to the top of the Glover tower along with some of the more dilute chamber acid. The "nitrated acid" trickling down the Glover tower loses the absorbed nitrous fumes and some water.

On leaving the Gay-Lussac tower the gases consist almost entirely of the nitrogen of the air used for the burning of the pyrites. These gases pass to a chimney, thus creating a partial vacuum which draws the gases through the plant.

### Tower Systems of Sulphuric Acid Manufacture

It has been mentioned above that in the ordinary chamber process one of the functions of the Glover tower is partly to oxidize the sulphur dioxide from the burner gases—in fact to do a portion of the work for which the lead chambers are provided. In point of fact, the action taking place in the Glover tower is several times more intense than that which occurs in an equal volume of chamber space.

Attempts have accordingly been made to dispense with the use of lead chambers and confine the production of sulphuric acid to towers, like the Glover tower, down which passes sulphuric acid containing dissolved oxides of nitrogen and up which the burner gases (sulphur dioxide, oxygen, etc.) are passing. The sulphuric acid is produced in a similar way to its formation in chambers, but in the liquid

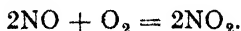
instead of the gaseous state, with consequent very considerable saving of space. This system is now a commercial proposition and has been operated with success to a limited extent on the Continent.

The details of the operations vary with different systems, but the following outline is more or less representative. Six towers are erected, the first five of which act like Glover towers, being fed with sulphuric acid charged with oxides of nitrogen, and being kept hot. The last tower acts as a Gay-Lussac tower and absorbs any oxides of nitrogen escaping from the previous towers. It is kept cool.

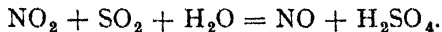
The chief disadvantages of tower systems over the older chamber process are the necessity (i) for pumping large volumes of acid, and (ii) of forcing large quantities of gas against the resistance of the tower packing. However, now that mechanically efficient yet acid-resisting pumping machinery is available, the former difficulty has largely disappeared, and the increased cost of power for both pumping operations is more than offset by the reduced capital cost, the smaller amount of space required and the greater efficiency of the tower system.

In spite of a large amount of investigation into this process the exact nature of the reactions on which the chamber process depends is still uncertain.

According to an old theory, nitric oxide, NO, unites with the oxygen from the air, forming nitrogen peroxide:



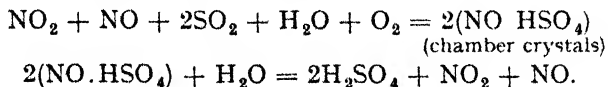
The nitrogen peroxide then oxidizes the sulphur dioxide, and is at the same time reduced to nitric oxide:



The nitric oxide is again oxidized to the peroxide, and so the cycle commences anew.

The nitrogen oxides thus serve to transfer oxygen from the air to the sulphur dioxide.

In some quarters this simple explanation is not accepted, and it is believed by many that an intermediate compound is formed, particularly since experiment shows that if the supply of steam or water be insufficient, crystals of **nitrosyl hydrogen sulphate** (the so-called **chamber crystals**) are formed. This acid decomposes with water, giving sulphuric acid and oxides of nitrogen:



Various other intermediate compounds have been suggested, but it seems best in the present state of our knowledge not to assume any more complicated series of reactions than the simple scheme suggested

above. In any case, the fact that a definite compound can be isolated by altering the conditions under which a reaction progresses is not proof that the compound so isolated is necessarily an intermediate compound when the reaction progresses under other conditions.

Chamber acid is now only used as such, but prior to the advent of

the contact process, the concentrated acid of commerce was made by concentrating chamber acid. Weak sulphuric acid left over from nitration processes for the production of explosives and similar processes is still concentrated so that it may be used again and special plant has been devised for this purpose.

Among the various types devised may be mentioned the **Kessler apparatus** and the **Gaillard Tower**.

In the **Kessler method** the weak acid is fed down a tower *R* (Fig. 24.13), which contains a number of perforated plates having inverted cups over the perforations, on to a "dish" of acid-resisting stone. Hot gases from a coke furnace are driven across the dish *S* and then up the tower *R*. The concentration of the acid in the dish produces a good deal of acid "fume" which is condensed in the tower, where the temperature is kept at such a point that steam escapes, but sulphuric acid does not. The issuing gases are then passed through a vessel packed with coke drenched with concentrated sulphuric acid which removes any remaining mist of acid droplets.

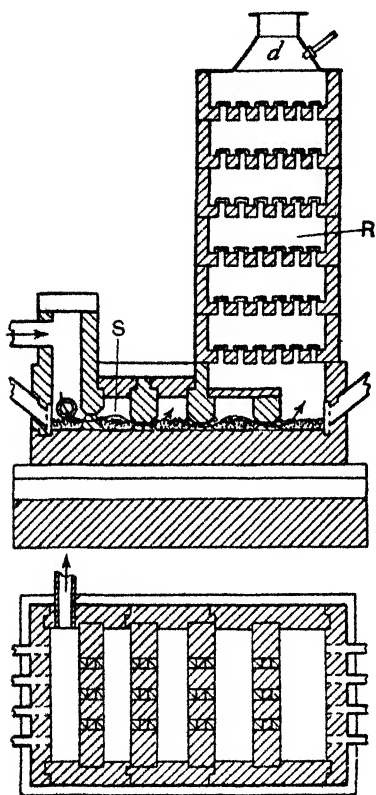


FIG. 24.13 —Kessler Plant  
(after Partington)

The **Gaillard Tower** (Fig. 24.14) is perhaps the most successful method, particularly when large quantities of acid have to be dealt with. It comprises a tower of acid-resisting stone or brick into the top of which a very fine spray of the acid to be concentrated is introduced. In the tower this spray meets a current of hot gases from a coke furnace. Progressive concentration of the acid takes place as it passes down the furnace, and a strong acid is run off from the bottom. The fumes carried off by the hot gases then pass up another, smaller lead tower down which some more of the acid to be concentrated is sprayed. The

fumes then pass to a chamber containing lead bars maintained at a high potential where the mist of acid droplets is "precipitated" and returned to the process.

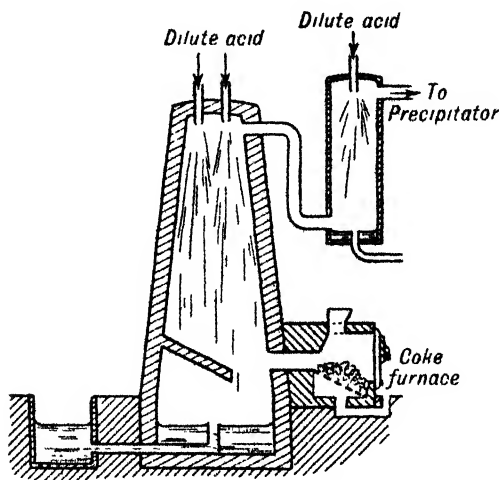
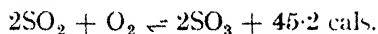


FIG 24 14 — Gaillard Tower

### § 30 The Contact Process

Sulphur dioxide and oxygen combine to some extent when heated alone, forming sulphur trioxide. The reaction, which may be represented by the equation:



is exothermic and hence, according to the principle of Le Chatelier (page 247), the amount of sulphur trioxide present at equilibrium will diminish as the temperature is raised. The reaction is, however, very slow, in the absence of a catalyst, but, as was shown by Peregrine Phillips in 1831, platinum is a very efficient catalyst for this reaction, and at temperatures of  $400^\circ$ – $500^\circ$  almost complete conversion of sulphur dioxide into sulphur trioxide can be effected in a reasonable time. At lower temperatures than this, the reaction is too slow, and at higher the amount of sulphur trioxide formed diminishes, falling almost to zero above  $1000^\circ$ .

This reaction is the basis of the **contact process** for the manufacture of sulphuric acid, since sulphur trioxide will combine with water, forming sulphuric acid.

The details of the process are illustrated by Fig. 24.15.

Sulphur dioxide is obtained in a manner similar to the chamber process, but requires very much more thorough purification in order to

avoid "poisoning" of the catalyst. It is particularly necessary for the gases to be absolutely free from arsenic.

The gases are cleaned by passage through a chamber—the "dust chamber"—into which steam is injected; through a water cooler and through a Glover tower in each of which the gases meet a descending spray of water, which removes chlorine and, in plant deriving sulphur dioxide from zinc sulphide concentrates, a good deal of lead sulphate is washed out.

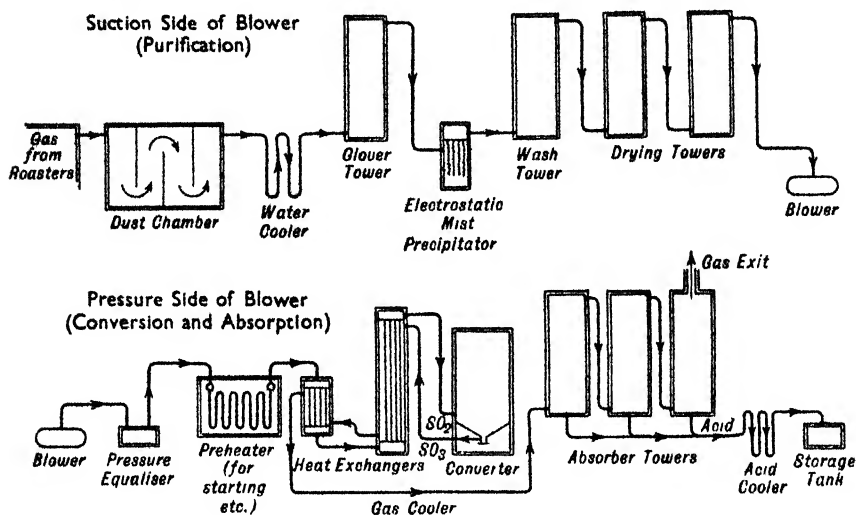


FIG. 24.15 —Contact Process

The last traces of suspended matter are removed by a Lodge-Cotterell electrostatic mist precipitator. This consists of vertical earthed lead tubes down the centre of each of which is a lead-covered wire at a potential of  $-20,000$  volts. This drives the negatively charged mist particles to the walls of the tube. The gases are then passed to a tower where they are showered with lime-water to remove last traces of chlorine and dried by passage through towers where they meet descending streams of concentrated sulphuric acid. Finally they pass through water to remove any sulphuric acid from the towers. The gases are periodically tested for dust, arsenic, etc., to make sure the scrubbers, etc., are working efficiently.

The purified gases then pass through a heat interchanger where they are heated up by the outcoming gases (which are themselves thereby cooled) and then through the catalyst chamber. Sulphur trioxide is formed and heat is evolved. The rate of flow is so arranged that the temperature in the catalyst chamber is kept at about  $400^\circ$ .

The exit gases consist principally of sulphur trioxide and nitrogen;

on cooling, the former forms a mist of very fine droplets which is absorbed with great difficulty by water or dilute sulphuric acid; but it is rapidly and completely absorbed by 98.5 per cent sulphuric acid. Hence the gases which leave the contact chamber pass into cast-iron tanks containing sulphuric acid of this strength. A stream of water or dilute acid is run into the condensing tanks at such a rate that the strength of the acid is maintained at 98.5 per cent. By restricting the supply of water in this operation, **oleum** or fuming sulphuric acid is obtained.

Formerly, platinum was almost the only catalyst used, being employed either in the form of platinized asbestos or deposited on magnesium sulphate or on silica gel, but it has now been superseded by vanadium pentoxide which is cheaper, more robust and less sensitive to poisoning than platinum; it is, however, still necessary to remove all small particles from the gas stream. Furthermore, if small quantities of halogen are allowed to remain they form volatile vanadyl compounds resulting in removal of catalyst in the effluent. Ferric oxide which is used in the *Mannheim process* is not sensitive to poisonous impurities, e.g., arsenic; indeed, it actually absorbs arsenic and so acts as a purifying agent. But it requires a higher temperature (about 700°) to do its work, and the oxidation is incomplete (50 to 60 per cent).

### The Anhydrite Process

The steadily increasing world demand for sulphuric acid has led to a serious shortage of sulphur and as, in this country, sulphur or sulphide ores (the principal sources of sulphur for sulphuric acid manufacture) have all to be imported, increasing attention has been paid lately to the use of anhydrite (calcium sulphate), which is indigenous in this country, as a source of sulphur dioxide.

This process has been developed to the point where substantial quantities of sulphuric acid are now being manufactured from anhydrite. The process consists in grinding together, in ball mills, a mixture of anhydrite, coke breeze and clay in suitable proportions to give a very finely divided intimate mixture of these substances. The mixture is then heated in large rotary kilns (about 225 feet long and 11 feet in diameter) of the type used in cement manufacture (page 700). The heating is effected by the combustion of powdered coal blown into the hot end of the kiln; the highest temperature reached is about 1400°. The exit gases contain about 9 per cent of sulphur dioxide and are subjected to the same sort of process of purification as described for the contact process. The purified sulphur dioxide is then converted into sulphuric acid by the contact process.



The quicklime formed combines with the clay present to form a cement clinker which is also marketed.

### § 31 Properties of Sulphuric Acid

Sulphuric acid is a colourless oily liquid, without odour. It is *extremely corrosive* to the skin and all the body tissues, and so causes very serious burns. Its density is 1.834 at 18°, and it freezes at 10.5°. The ordinary concentrated acid of the laboratory contains about 2 per cent of water and, therefore, freezes at a very much lower temperature. It boils with decomposition; giving off choking fumes of sulphur trioxide and the vapour of the acid.

On mixing sulphuric acid with water the mixture becomes hot and the temperature may rise as high as 120°. This is liable to cause serious accidents if care be not taken when diluting sulphuric acid. The acid should always be added to the water, in a thin stream, with vigorous stirring.

When sulphuric acid is mixed with water, the volume of the cold mixture is much less than the sum of the volumes of water and acid used. The greatest contraction occurs with a solution containing about 97.7 per cent of  $\text{H}_2\text{SO}_4$ .

Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) boils at about 273° with partial decomposition. Some sulphur trioxide passes off as vapour; the acid in the retort becomes weaker, and the boiling point steadily rises until the acid has attained a strength of 98.3 per cent  $\text{H}_2\text{SO}_4$  when it distils over unchanged. Conversely, on boiling dilute solutions of sulphuric acid, the acid becomes stronger and stronger since water or very dilute acid passes over; at the same time, the boiling point steadily rises until the acid has attained a strength of 98.3 per cent  $\text{H}_2\text{SO}_4$ , when it distils over unchanged, at 338°.

The specific gravity curve shows a maximum, or the contraction curve a minimum with an acid of approximately this same concentration. This acid also absorbs sulphur trioxide more rapidly than either water or dilute sulphuric acid.

The freezing-point curves of mixtures of sulphur trioxide and water are shown in Fig. 24.16. Maxima occur at points corresponding to the compositions  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (m.p.  $-28.2^\circ$ );  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (m.p.  $-39.5^\circ$ ); and  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (m.p.  $8.5^\circ$ ). Evidence has also been brought forward by Gable (1950) which suggests the existence of a hydrate of the composition  $\text{H}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  (m.p. about  $-37^\circ$ ).

The application of the Phase Rule (page 185) to freezing-point curves shows that these may be taken to represent the composition of definite compounds formed under the conditions stated.

The great affinity of sulphuric acid for water makes it a useful drying agent. Hence its use in desiccators, and for drying gases. Sulphuric acid acts upon solid and liquid substances depriving them of water; or even decomposing the substance—splitting off the elements of water when no ready-formed water is present. Wood, paper, sugar, starch, and many organic substances are blackened by concentrated sulphuric acid owing to the separation of carbon which accompanies the removal



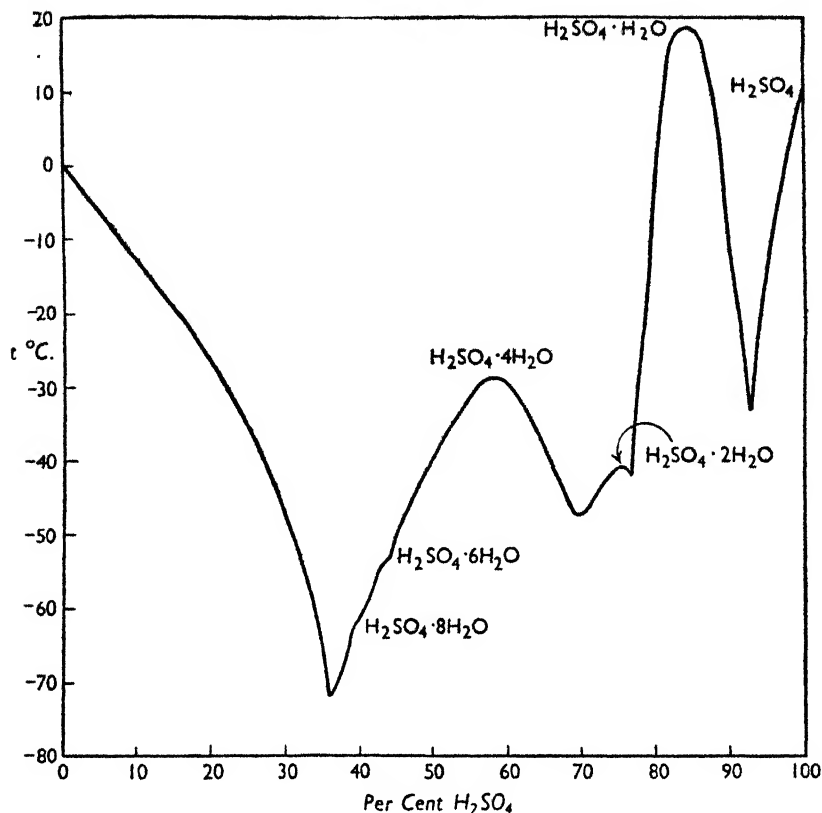


FIG. 24 16 — Freezing-point Curve  
(From Barnett and Wilson, *Inorganic Chemistry*)

of the elements of water. This property is utilized for the preparation of carbon monoxide (page 398). The effect is easily demonstrated by stirring 10 grams of powdered cane sugar with 12 grams of concentrated sulphuric acid in a beaker. The sugar first becomes pale brown, rapidly darkens in tint, and finally becomes black; at the same time, much steam is evolved and the mass swells up considerably.

Dilute sulphuric acid shows all the ordinary properties of a strong acid (page 341) such as turning litmus red, action on metals, etc. According to the Ionic Theory, it is not so strong an acid as nitric and hydrochloric acids, but is stronger than most others (page 268). The dilute acid reacts with all metals except bismuth, mercury, lead, copper and the noble metals, liberating hydrogen, e.g.,



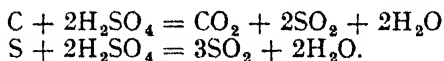
(Aluminium, chromium and nickel, which sometimes appear not to react, will do so if the protecting film of oxide is removed.)

Concentrated sulphuric acid does not react with metals in the cold, but when heated oxidizes them, being itself reduced to sulphur dioxide. This is owing to the fact that sulphuric acid, when hot, is an oxidizing agent.

A typical example of its action on metals has been discussed in connection with the laboratory preparation of sulphur dioxide (page 487), using copper. The reaction between concentrated sulphuric acid and other metals is probably similar.

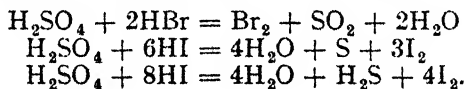
In the case of zinc, for example, hydrogen sulphide, zinc sulphide and free sulphur may be formed, as well as sulphur dioxide.

Many non-metals are also oxidized by sulphuric acid, e.g., carbon and sulphur:



Hydrogen also, even in the cold, is oxidized to a slight extent, forming traces of sulphur dioxide, a fact which has to be borne in mind when drying this gas with concentrated sulphuric acid.

Another familiar example of the oxidizing action of sulphuric acid is its behaviour with bromides and iodides (pages 561, 568). The hydrobromic and hydriodic acid first formed are oxidized to bromine and iodine respectively, so that these acids cannot be prepared by the action of concentrated sulphuric acid on their salts.



### § 32 Uses of Sulphuric Acid

Sulphuric acid is a very important industrial commodity and its uses are numerous. It was formerly used in very large quantities for making sodium carbonate and nitric acid, but the development of the ammonia-soda process and of the synthetic nitrate industry has reduced the demand for it for these purposes. It is also employed extensively for the manufacture of explosives, fertilizers (e.g., superphosphate and ammonium sulphate), alums, phosphorus, hydrogen fluoride, insecticides, synthetic detergents, rayon, cellophane, and dyestuffs. Large quantities are used in coal-tar and petroleum refining, in bleaching and dyeing operations, electro-plating, metallurgy, etc. The manufacture of sulphates such as sodium sulphate for the glass industry, and ferrous sulphate for ink manufacture, lead, zinc and titanium pigments also absorbs considerable quantities of the acid.

### § 33 Formula of Sulphuric Acid

The formula for sulphuric acid is generally taken to be  $\text{SO}_2(\text{OH})_2$  for the following reasons:

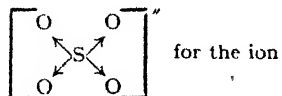
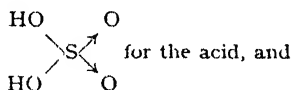
*First.*—It is a dibasic acid, i.e., it forms two series of salts and only two.

*Second.*—Chlorine can react with concentrated sulphuric acid, forming chlorosulphonic acid  $\text{Cl—HSO}_3$ , where one OH group in sulphuric acid is replaced by chlorine. Phosphorus pentachloride— $\text{PCl}_5$ —can displace two OH groups in sulphuric acid, forming sulphuryl chloride  $\text{Cl—SO}_2\text{—Cl}$ . Both these chloro-compounds react with water, forming sulphuric acid. The two OH groups can likewise be replaced by other radicals, e.g.,  $\text{NH}_2$ . Since two OH groups can be displaced together or separately, we infer that (1) sulphuric acid— $\text{H}_2\text{SO}_4$ —contains two hydroxyl—OH—groups.

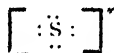
*Third.*—It is possible to make but one compound of the type,  $\text{CH}_3\text{O—SO}_2\text{—OK}$ , by replacing the hydrogen of the hydroxyl groups with the radicals like  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , etc. Hence it is inferred (2) the hydroxyl groups are related to the remainder of the atoms in the molecule  $\text{H}_2\text{SO}_4$  in a symmetrical manner.

*Fourth.*—Certain univalent hydrocarbon radicals— $\text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5$ , etc.—can replace the chlorine in  $\text{ClHSO}_3$  and in  $\text{SO}_2\text{Cl}_2$  to form, say, ethyl sulphonic acid— $\text{C}_2\text{H}_5\text{.SO}_2\text{.OH}$ , and diphenylsulphone— $(\text{C}_6\text{H}_5)_2\text{SO}_2$ , respectively. The same compounds can be made by the oxidation of mercaptan— $\text{C}_2\text{H}_5\text{SH}$ , and of diphenyl sulphide— $(\text{C}_6\text{H}_5)_2\text{S}$ , in which the radical must be joined directly to the sulphur atom. Assuming that the radicals remain fixed to the sulphur atom during the oxidation, it is inferred that (3) the hydroxyl groups in sulphuric acid— $\text{H}_2\text{SO}_4$ —are directly attached to the sulphur atom.

The detailed structures

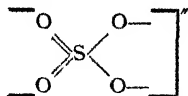


are in common use since they are in agreement with the "octet rule" and with the identical character of all four bonds in the ion. They also explain the relation between the sulphate ion and the sulphide ion

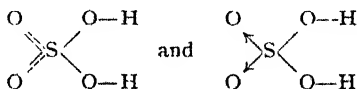


since the former may be supposed to be formed from the latter by donating four electron pairs to four oxygen atoms. Recently, determinations of the bond lengths have suggested the existence of a considerable proportion of double bond character

in the links which would imply resonance between the forms represented by the older formula



with the double bonds resonating among the oxygen atoms so making them equivalent, and the one given above. Similarly the non-ionized acid is regarded as a resonance hybrid of



X-ray analysis has shown that the oxygen atoms are tetrahedrally arranged round the sulphur atom

### § 34 Detection and Determination of Sulphuric Acid and Sulphates

The usual method of detection is to add dilute hydrochloric acid and barium chloride solution to a solution of the suspected sulphate. If a white precipitate be formed, it indicates the presence of a sulphate, owing to the formation of insoluble barium sulphate. It is essential to have the solution acid as many barium salts are insoluble in water, but, apart from the fluosilicate, the sulphate is the only one which is insoluble in hydrochloric acid.

The usual confirmatory test is to heat the suspected sulphate on charcoal with sodium carbonate, using the reducing flame, when a sulphide will be formed which when treated with a few drops of very dilute hydrochloric acid and covered with lead acetate paper produces a black stain of lead sulphide.

Sulphates are usually determined by slowly adding a dilute solution of barium chloride to a hot solution of the sulphate which has been slightly acidified with hydrochloric acid. The precipitated barium sulphate is filtered off, washed, heated to redness and weighed.

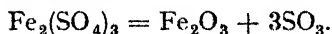
### § 35 Sulphates

Sulphuric acid forms salts known as the sulphates when it reacts with certain metals, metallic oxides, hydroxides or carbonates, and many of them are of considerable importance. These will be found described under the heading of the metal concerned.

Sulphates are also prepared by heating the salts of more volatile acids, such as hydrochloric and nitric acids, with sulphuric acid. Sulphuric acid is a dibasic acid and so readily forms two series of salts, viz., acid sulphates and normal sulphates. With certain poly-acid bases, basic sulphates also occur. There are many important double sulphates also, such as the alums (page 751).

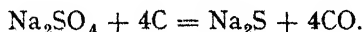
The sulphates are mostly fairly soluble in water and crystallize well, frequently with several molecules of water of crystallization. The sulphates of lead, calcium, strontium and barium are, however, only very sparingly soluble in water.

The sulphates of the alkali metals and alkaline earths are stable to heat, but those derived from weaker bases, especially those of trivalent metals, often decompose into the oxide of the metal and (usually) sulphur trioxide when heated strongly. As an example the old Nordhausen process for making fuming sulphuric acid (see below) involved the decomposition of ferric sulphate



Crystallized ferrous sulphate (page 496) gives sulphur dioxide when heated; this type of decomposition is unusual.

Most sulphates are reduced to sulphides when heated with carbon, e.g.,



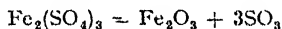
(Compare the manufacture of sodium sulphide—page 629.)

### § 36 Pyrosulphuric Acid, $\text{H}_2\text{S}_2\text{O}_7$ , and the Pyrosulphates

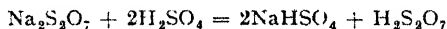
Mention has already been made (page 503) of the fact that sulphur trioxide will dissolve in concentrated sulphuric acid, forming what is often called **oleum** or **Nordhausen** or **fuming sulphuric acid**. A similar acid is obtained by distilling partially dehydrated ferrous sulphate crystals,  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  (preferably with a little sulphuric acid in the receiver). The reaction appears to be represented



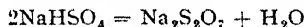
followed by



The same acid is obtained by heating sodium pyrosulphate with concentrated sulphuric acid



Sodium pyrosulphate is made by heating sodium bisulphate to about  $400^\circ$ .



hence the name *pyro* sulphuric acid—from the Greek  $\pi\rho$  (pyr), fire

Fuming sulphuric acid is a viscous, oily-looking liquid which is considered to be a solution of variable proportions of sulphur trioxide in concentrated sulphuric acid. The "fuming" of the acid is due to the escape of the sulphur trioxide. If the fuming acid be warmed, sulphur trioxide volatilizes and leaves sulphuric acid,  $\text{H}_2\text{SO}_4$ , behind. This acid has often a brownish colour owing to the presence of a little organic matter. It may also contain other impurities. Fuming sulphuric acid is used in refining petroleum, in the manufacture of dyes, explosives, shoe-blackening, etc.

The freezing-point curve of mixtures of sulphuric acid and sulphur trioxide is given in Fig. 24 17. A very pronounced maximum occurs at a composition corresponding to  $\text{H}_2\text{SO}_4 + \text{SO}_3$ , i.e. to a compound  $\text{H}_2\text{S}_2\text{O}_7$ , which melts at  $36^\circ$ . The curve shows the existence of two eutectics, one corresponding to the presence of 20 per cent of "excess" sulphur dioxide, the other to the presence of 65 per cent. These are the mixtures commonly sold as oleum since they are liquid at ordinary temperatures. If equal volumes of these two eutectic mixtures be mixed

at ordinary temperatures a solid crystalline mass of pyrosulphuric acid is at once formed.

Salts known as the pyrosulphates, do appear to exist (cf the sodium salt mentioned above) and so it seems probable that the acid is definitely  $\text{H}_2\text{S}_2\text{O}_7$ ,

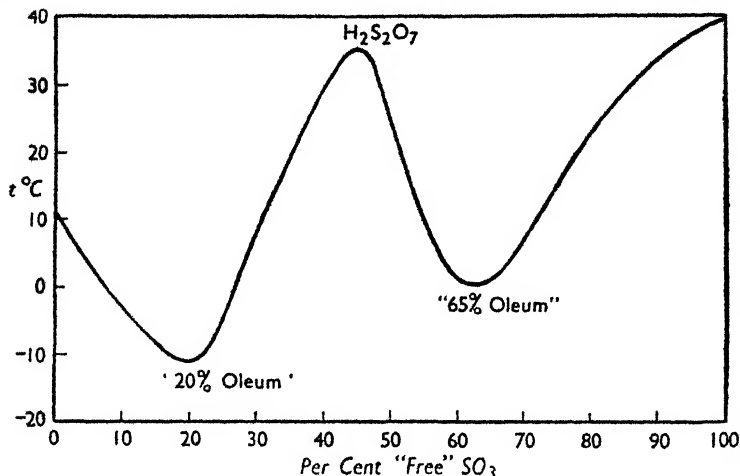


FIG 24 17 Freezing point curve of  $\text{H}_2\text{SO}_4 + \text{SO}_3$   
(From Barnett and Wilson *Inorganic Chemistry*)

### § 37 Persulphuric Acids and Persulphates

It will be remembered (page 301) that when dilute sulphuric acid is electrolysed hydrogen and oxygen are obtained in the proportion of two volumes of hydrogen and one volume of oxygen. As the concentration of the acid is increased less and less oxygen is evolved until with 50 per cent sulphuric acid and a cold solution inappreciable quantities of oxygen will be disengaged at the anode. A new compound is formed—persulphuric acid  $\text{H}_2\text{S}_2\text{O}_8$ . The best way of studying this action is to electrolyse a saturated solution of potassium sulphate in sulphuric acid specific gravity about 1.3.

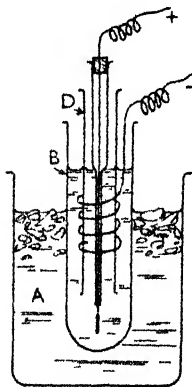


FIG 24 18  
Preparation of  
Potassium Persulphate

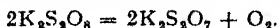
The solution is placed in a test tube *B* (Fig 24 18) so that the test tube is about three fourths filled. A glass cylinder *D* is fixed in the test-tube. A coil of platinum wire—the cathode—is allowed to dip into the solution of potassium sulphate as indicated in the diagram, and a platinum wire sealed to a piece of glass tube so that about  $1\frac{1}{2}$  to 2 cm of the wire projects from the tube, forms the anode. This is fixed within the cylinder. The large beaker is filled with water *A* in which pieces of ice are floating. A current of about one or two amperes is sent through the solution. Hydrogen appears at the cathode and a white crystalline mass accumulates at the anode.

The formula  $\text{K}_2\text{S}_2\text{O}_8$  is conformable with the change in the molecular conductivity of solutions of the salt with dilution and with the lowering of the freezing point of

solutions of the salt. H. Marshall, who first isolated potassium persulphate in 1891, suggested the formula  $\text{KSO}_4$ , but later favoured the doubled formula given above.

### The Properties of Persulphates

The solid persulphates are fairly stable. Potassium persulphate decomposes on heating into potassium pyrosulphate and oxygen:

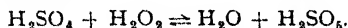


An aqueous solution of a persulphate is a powerful oxidizing agent, and is used for that purpose in analytical work, e.g., it precipitates brown hydrated manganese dioxide from soluble manganese salts. The persulphates *slowly* liberate iodine from solutions of potassium iodide; oxidize iodine to iodic acid, etc. A solution of a manganese salt gives a precipitate of manganese dioxide with potassium persulphate; but, in the presence of silver nitrate, is oxidized to pink permanganate—*Marshall's reaction*.

Barium persulphate is readily soluble in water. Hence barium chloride gives no precipitate with the persulphates, although it does give a precipitate with a sulphate, but if the persulphate be decomposed by warming, a precipitate of barium sulphate is obtained. A dilute solution of the acid—**persulphuric acid**, also called **perdisulphuric acid**—can be made by treating the barium persulphate with sulphuric acid. The persulphates are used in photography for "reducing" negatives; and ammonium persulphate is used in technical organic chemistry as well as in the manufacture of hydrogen peroxide (page 322).

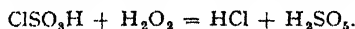
### Caro's Acid

If potassium persulphate be digested with 40 per cent sulphuric acid in a freezing mixture so that there is no rise of temperature, or if concentrated sulphuric acid and hydrogen peroxide (5 per cent) be mixed together, a **permonosulphuric acid** is obtained.



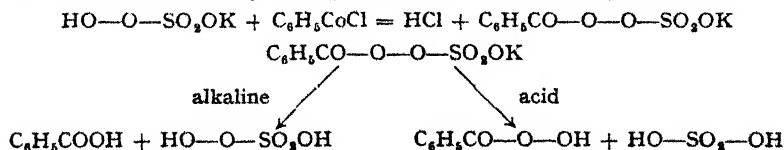
This acid is sometimes called Caro's acid,  $\text{H}_2\text{SO}_5$ —after its discoverer, N. Caro, 1898.

The solid acid is best obtained by the action of chlorosulphonic acid on anhydrous hydrogen peroxide

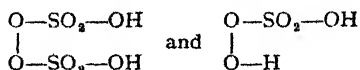


The pure acid forms a white crystalline mass which melts at about  $45^\circ$ , and it is comparatively stable. Like persulphuric acid, Caro's acid has strong oxidizing qualities. Unlike persulphuric acid, it liberates iodine from potassium iodide *at once*. It also oxidizes sulphur dioxide to the trioxide; ferrous salts to ferric salts; hydrogen chloride to chlorine, but it is without action on hydrogen fluoride; and precipitates peroxides from salts of silver, copper, manganese, cobalt, and nickel. It does not bleach permanganates, nor oxidize chromic or titanium salts, and is therefore distinct from hydrogen peroxide.

There has been some discussion whether Caro's acid is monobasic,  $\text{H}_2\text{SO}_5$ , or dibasic,  $\text{H}_2\text{S}_2\text{O}_8$ . The analysis of the potassium salt is not conclusive, since  $\text{KHSO}_5$  would have the same ultimate composition as the salt  $\text{K}_2\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$ . Benzoyl chloride,  $\text{C}_6\text{H}_5\text{CO} \cdot \text{Cl}$ , reacts with the potassium salt of Caro's acid, forming the benzoyl derivative which, on alkaline hydrolysis, gives Caro's acid and benzoic acid and on acid hydrolysis gives sulphuric acid and perbenzoic acid. This reaction undoubtedly corresponds with the monobasicity of the acid:



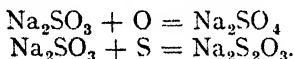
The synthesis of Caro's acid by the action of the calculated quantity of chlorosulphonic acid,  $\text{SO}_2\text{Cl}(\text{OH})$ , on pure hydrogen peroxide in the cold is also in agreement with the view of the molecular formula just indicated. On this basis persulphuric acid and Caro's acid are represented by the formulae



respectively, that is, as the disulphonate and monosulphonate of hydrogen peroxide.

### § 38 Thiosulphuric Acid and the Thiosulphates

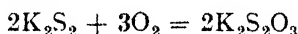
If an aqueous solution of sodium sulphite,  $\text{Na}_2\text{SO}_3$ , be exposed to the air, one oxygen atom per molecule of sodium sulphite is slowly taken up, and sodium sulphate,  $\text{Na}_2\text{SO}_4$ , is formed. Similarly, if sodium sulphite be digested with finely divided sulphur for some time, one atom of sulphur per molecule of sodium sulphite is taken up, and a new salt, sodium thiosulphate,  $\text{Na}_2\text{S}_2\text{O}_3$  (page 632) is formed:



These reactions suggest some analogy in the structure of the thiosulphates and the sulphates; and this is emphasized by the term *thio*-sulphates, meaning *sulpho*-sulphates—from the Greek *θειον* (*theion*), sulphur.

The name *sodium hyposulphite* (the photographer's "hypo") was formerly used for this salt, but that name properly belongs to the substance  $\text{Na}_2\text{S}_2\text{O}_4$ .

Thiosulphates are also formed by the action of caustic alkalis on sulphur (page 479), and by the oxidation of soluble sulphides (e.g., potassium sulphides) in air:

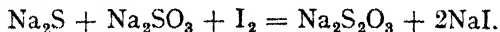


and also, by the action of sulphur dioxide on sodium sulphide:



Thiosulphates were formerly manufactured from alkali waste (calcium sulphide produced in the now obsolete Leblanc process for making sodium carbonate) but are now made from the waste liquors from the production of sodium sulphide (page 629).

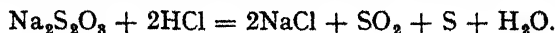
Sodium thiosulphate is also formed when a mixture of sodium sulphide and sulphite is treated with iodine. This is sometimes called *Spring's reaction* (cf. page 515).



Thiosulphuric acid has not been isolated. By acting on a thiosulphate with a dilute mineral acid, thiosulphuric acid appears to be formed, but it begins to decompose at once into sulphur dioxide and



free sulphur. The sulphur only appears after the lapse of a certain time, seconds or minutes, according to the concentration of the solution:



The evolution of sulphur dioxide with the separation of sulphur, on the addition of a dilute mineral acid, distinguishes thiosulphates from sulphites in qualitative analysis.

### § 39 Other Oxides of Sulphur

In addition to sulphur dioxide and sulphur trioxide, which have been described above, the following oxides of sulphur have been reported:

Sulphur monoxide,  $\text{SO}$ .  
 Sulphur sesquioxide,  $\text{S}_2\text{O}_3$ .  
 Sulphur tetroxide,  $\text{SO}_4$ .  
 Sulphur heptoxide,  $\text{S}_2\text{O}_7$ .

These are, however, not of any very great importance at this stage of our work.

#### Sulphur Monoxide, $\text{SO}$

The isolation of this oxide is claimed by Schenk (1932) by the action of an electric discharge on a mixture of sulphur dioxide and sulphur at low pressures. More recently (1935) he has obtained it (mixed with sulphur dioxide) by the combustion of sulphur under suitable conditions.

It is described as a colourless gas which decomposes very easily, particularly in the presence of water or organic matter. It combines with oxygen when sparked, giving sulphur dioxide, while with metals it forms sulphides.

#### Sulphur Sesquioxide, $\text{S}_2\text{O}_3$

This oxide is supposed to be formed as a malachite-green crystalline mass by the direct union of sulphur and sulphur trioxide, and as a blue solution by the action of flowers of sulphur on Nordhausen sulphuric acid. There is some doubt whether the bluish-green mass is a mixture or a compound. With water, sulphur sesquioxide gives sulphur and a mixture of sulphuric and sulphurous acids, and not hyposulphurous acid. This does not prove that sulphur sesquioxide is not the anhydride of hyposulphurous acid because the latter decomposes in a similar way (see page 514 below).

#### Sulphur Tetroxide, $\text{SO}_4$

This oxide is claimed to have been isolated in 1934 by Schwarz and Achenbach by the action of a glow discharge on a mixture of sulphur dioxide and a large excess of oxygen at 0.5 mm. pressure. It is described as a white solid which begins to decompose at  $-5^\circ$  and melts at  $3^\circ$ , forming sulphur heptoxide. It is said to be a good oxidizing agent.

#### Sulphur Heptoxide, $\text{S}_2\text{O}_7$

M. Berthelot (1878) found that when a mixture of oxygen and sulphur dioxide is exposed to the action of a silent discharge (cf. preparation of ozone, page 348), a colourless crystalline substance said to be sulphur heptoxide is formed:



The crystals do not fume in moist air and, when added to cold water, float on it for a little time before forming a solution with strong oxidizing properties. It gradually decomposes, on keeping, into sulphur trioxide and oxygen.

### § 40 Other Acids derived from Sulphur

Besides the important acids already discussed, the following derived from sulphur are known:

Sulphoxylic acid,  $\text{H}_2\text{SO}_3$   
(in the form of its cobalt salt and of organic derivatives only);

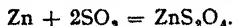
Hyposulphurous acid  
(hydrosulphurous acid),  $\text{H}_2\text{S}_2\text{O}_4$ ;

The Polythionic Acids,  $\text{H}_2\text{S}_n\text{O}_6$   
( $n = 2, 3, 4, 5$  or  $6$ ).

#### Hyposulphurous Acid, $\text{H}_2\text{S}_2\text{O}_4$

C. L. Berthollet (1789) noticed that iron dissolves in sulphurous acid without giving off a gas; L. N. Vauquelin and A. F. Fourcroy (1798) found that tin and zinc behaved in a similar way; and C. F. Schonbein (1852) obtained some reactions with a lower sulphur acid which were probably caused by what is now called hyposulphurous acid. P. Schutzenberger discovered this acid in 1869.

Commercially, *sodium hyposulphite* is made by treating an aqueous solution of sulphur dioxide with finely divided zinc. Zinc hyposulphite is obtained:



The zinc is precipitated by means of sodium carbonate, or caustic soda, solution and on saturating the filtrate with common salt, sodium hyposulphite crystallizes out as the dehydrate,  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . This is dehydrated and washed with alcohol; the anhydrous salt keeps better than the hydrated form.

The free acid can be obtained as a yellow solution by treating calcium hyposulphite with oxalic acid. It readily absorbs oxygen from the air and is a very powerful reducing agent.

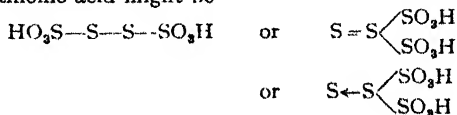
The sodium salt is used industrially, and in the chemical laboratory as a reducing agent. For instance, it bleaches sugar, indigo blue, etc. It reduces permanganates; and also reduces some metallic salts to the metal—e.g., silver nitrate, and gold and platinum chlorides; and in the case of copper sulphate, a brown copper hydride,  $\text{CuH}$ , is formed. It seems to act as an oxidizing agent towards hydrogen sulphide in the presence of moisture, for sulphur is precipitated, and thiosulphate is formed.

The hyposulphites are known commercially as hydrosulphites, since hypsulphurous acid is an old name for thiosulphuric acid (q.v.), and although the use of the term hyposulphite for the salts of the latter acid has been largely given up, it is still retained by photographers, hence giving rise to the possibility of confusion.

### § 41 The Polythionic Acids

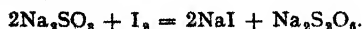
There is a remarkable series of five acids—called collectively the polythionic acids—which have the general formula  $\text{H}_2\text{S}_n\text{O}_6$ .

They are usually discussed as a group but, in fact, they form three distinct groups. Thus, dithionic acid ( $\text{H}_2\text{S}_2\text{O}_6$ ) has been shown by X-ray examination to have the structure  $\text{HO}_3\text{S}-\text{SO}_3\text{H}$ ; trithionic acid, similarly, is known to be the disulphonate of hydrogen sulphide,  $\text{HO}_3\text{S}-\text{S}-\text{SO}_3\text{H}$ , while the structure of the higher acids, which form a third group, is not definitely known. They may have sulphonic groups attached either to one, or to both, ends of a chain of sulphur atoms. Thus, for instance, tetrathionic acid might be



**Dithionic Acid,  $\text{H}_2\text{S}_2\text{O}_4$** 

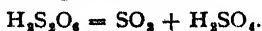
The sodium salt is made together with some sulphuric acid, by Spring's reaction with iodine on sodium sulphite:



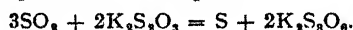
The manganese salt,  $\text{MnS}_2\text{O}_4$ , is made by passing sulphur dioxide through water with manganese dioxide in suspension:



Ferric hydroxide or cobaltic hydroxide forms ferrous or cobaltous sulphate and dithionate when treated with sulphurous acid at a low temperature. Manganese dithionate is converted into barium dithionate,  $\text{BaS}_2\text{O}_6$ , by mixing it with barium hydroxide,  $\text{Ba}(\text{OH})_2$ , and the resulting salt can be purified by crystallization:  $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  is formed. This gives soluble dithionic acid and insoluble barium sulphate when treated with dilute sulphuric acid. The aqueous solution of the acid can be concentrated by evaporation until its specific gravity is about 1.35, any further concentration decomposes the acid:

**Trithionic Acid,  $\text{H}_2\text{S}_3\text{O}_6$** 

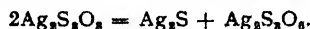
The potassium salt of this acid is formed by passing sulphur dioxide through a concentrated solution of potassium thiosulphate:



Sodium trithionate is also formed by the action of sulphur chloride,  $\text{SCl}_2$ , on sodium sulphite, and by warming an aqueous solution of potassium hydrogen sulphite with flowers of sulphur:



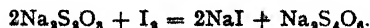
By boiling silver thiosulphate with water, a molecule of  $\text{Ag}_2\text{S}$  splits from two molecules of the thiosulphate and silver trithionate remains:



The acid itself is formed from the potassium salt by the addition of hydrofluosilicic acid. Potassium fluosilicate is precipitated, and the trithionic acid remains in solution. The acid and its salts are readily decomposed into sulphur, and sulphuric acid or a sulphate. By the reducing action of sodium amalgam, sodium trithionate is converted back into sodium sulphite and sodium thiosulphate. According to Chancel and Deacon, when a solution of sodium trithionate is boiled with sodium sulphide, sodium thiosulphate is formed. There is thus an intimate relation between thiosulphuric and trithionic acids.

**Tetrathionic Acid,  $\text{H}_2\text{S}_4\text{O}_6$** 

The sodium salt is formed by Spring's reaction with iodine and sodium thiosulphate:



The barium salt is prepared in a similar manner, and from this the acid itself is obtained by the action of dilute sulphuric acid. The reaction under consideration is the last of the set of condensations by the removal of an atom of sodium from each of two molecules of a salt and the condensation of the residues to form a more complex molecule—with sodium thiosulphate, di-, (tri-), and tetrathionate. All these reactions are reversed and the original salts reproduced by treating the complex salts with sodium amalgam. Tetrathionic acid can be made by passing a current of hydrogen sulphide into sulphurous acid until the smell of sulphur dioxide is discharged. The solution can be warmed on a water-bath to get rid of sulphur dioxide and hydrogen sulphide; the water lost by evaporation being replaced from time to time.

When hydrogen sulphide is passed into a concentrated solution of sulphurous acid at  $0^\circ$ , a solution containing a number of the polythionic acids is formed. It is called **Wackenroder's solution**. The existence of polythionates was first revealed by the study of Wackenroder's solution. Tetrathionic acid and pentathionic acid are important constituents of this solution but other polythionates are also present as well as sulphurous and hydrosulphurous acids and colloidal sulphur. Wackenroder's solution has been the subject of much investigation but the nature of the reactions involved is still in doubt.

The best method for the preparation of **pentathionic acid** is by the spontaneous decomposition of thiosulphuric acid solution below  $0^\circ$  in presence of a little arsenious oxide. The acid itself cannot be isolated but **potassium pentathionate** can be obtained by addition of potassium hydroxide followed by crystallization. The crystals which separate have the empirical composition:  $K_2S_5O_6 \cdot 3H_2O$ .

**Potassium hexathionate**,  $K_2S_6O_8$ , corresponding with the unknown **hexathionic acid**,  $H_2S_6O_8$ , is said to have been prepared in an impure condition from the mother liquid remaining after the separation of potassium pentathionate. The aqueous solution is very unstable.

### § 42 Acid Halides of Sulphur

Acid halides are compounds derived from oxyacids by the replacement of one or more hydroxyl groups by halogen. A whole series of such acid halides are derived from the sulphur acids. Thus, from sulphurous acid, there are:

Thionyl fluoride,  $SOF_2$ ,  
Thionyl chloride,  $SOCl_2$ ,  
Thionyl bromide,  $SOBr_2$ ;

and, derived from sulphuric acid,

Sulphuryl fluoride,  $SO_2F_2$ ,  
Sulphuryl chloride,  $SO_2Cl_2$ ,  
Fluorosulphonic acid,  $HO \cdot SO_2F$ ,  
Chlorosulphonic acid,  $HO \cdot SO_2Cl$ .

Only thionyl chloride, sulphuryl chloride and chlorosulphonic acid are of any great importance.

The remaining possible compounds of bromine and of iodine corresponding to the thionyl and sulphuryl compounds are either unknown or, if their preparation has been described, their existence is very doubtful.

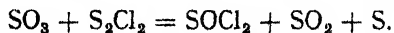
### § 43 Thionyl Halides

#### Thionyl Chloride, $SOCl_2$

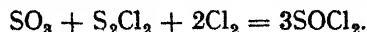
Thionyl chloride can be prepared by the action of phosphorus pentachloride on sulphur dioxide or sodium sulphite:



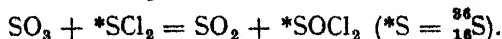
It is also formed by the action of sulphur monochloride on sulphur trioxide:



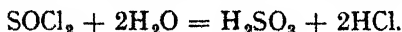
The first of these methods is often employed in the laboratory; the last is the usual commercial process, with the modification that chlorine is passed through the mixture in order that the free sulphur formed may be reconverted into sulphur chloride, the over-all reaction then being



It is interesting to note that if the reaction be carried out with sulphur dichloride containing a radioactive isotope of sulphur ( $^{36}_{16}\text{S}$ ) the radioactivity is found in the thionyl chloride and not as might have been expected in the sulphur dioxide:



Thionyl chloride is a colourless liquid, which fumes in air and boils at  $78.8^\circ$ . It is hydrolysed by water, forming sulphurous acid, and hence is considered to be the acid chloride of sulphurous acid:



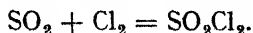
It finds employment in the laboratory for the replacement of hydroxyl groups by chlorine, since it reacts with hydroxy compounds in a manner similar to phosphorus halides, while having the advantage of giving a gaseous and easily removed by-product, viz., sulphur dioxide. It is used commercially for this purpose in the manufacture of the acid chlorides of organic acids.

**Thionyl fluoride** is formed by the action of arsenic or antimony trifluoride on thionyl chloride, and **thionyl bromide** by treating thionyl chloride with excess of gaseous hydrogen bromide. Thionyl fluoride is a colourless gas which fumes in air, thionyl bromide is an orange liquid which boils at  $138^\circ$  with decomposition. The reactions of both compounds are similar to those of thionyl chloride.

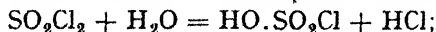
#### § 44 Sulphuryl Compounds

##### Sulphuryl Chloride, $\text{SO}_2\text{Cl}_2$

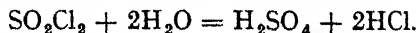
If a mixture of sulphur dioxide and chlorine be exposed to direct sunlight, especially if a little camphor be present, sulphuryl chloride is obtained:



It is a colourless liquid, which boils at  $69^\circ$ . It reacts with water in two stages. With a little water, chlorosulphonic acid is formed:



while, with excess of water, sulphuric acid results:



These reactions indicate that sulphuryl chloride is the acid chloride of sulphuric acid.

It is used commercially in the manufacture of organic acid chlorides and is finding increasing use in organic chemistry as a sulphonating agent.

**Sulphuryl fluoride,  $\text{SO}_2\text{F}_2$** , has been obtained similarly by the direct union of sulphur dioxide and fluorine, but is best made by heating barium fluorosulphonate



It is a colourless gas and behaves in an analogous manner to the chloride.

### **Fluorosulphonic Acid, $\text{HO} \cdot \text{SO}_2\text{F}$**

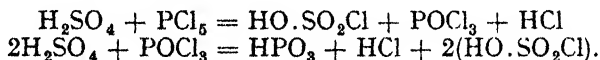
This compound can be readily obtained by distilling calcium fluoride with oleum. It is hydrolysed by cold water but not so readily as chlorosulphonic acid. Salts of fluorosulphonic acid are soluble in water and can be recrystallized if the process is carried out quickly and the water is not too hot. Some fluorosulphonates, such as the lithium salt, are soluble also in organic solvents.

### **Chlorosulphonic Acid, $\text{HO} \cdot \text{SO}_2\text{Cl}$**

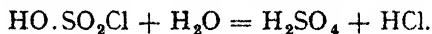
This acid can be made by direct union of sulphur trioxide and hydrogen chloride:



or by distilling a mixture of concentrated sulphuric acid with phosphorus pentachloride or oxychloride:



Chlorosulphonic acid is a colourless liquid which fumes in air and which boils at  $152^\circ$ . It reacts with water with explosive violence, forming a mixture of sulphuric and hydrochloric acids:



It finds extensive use in organic chemistry both technically (e.g., in the manufacture of saccharine) and in the laboratory.

## **§ 45 Sulphur Halides**

The following halides of sulphur are known with reasonable certainty to exist:

Sulphur hexafluoride,  $\text{SF}_6$ ,  
 Sulphur decafluoride,  $\text{S}_2\text{F}_{10}$ ,  
 Sulphur monofluoride,  $\text{S}_2\text{F}_2$ ,  
 Sulphur monochloride,  $\text{S}_2\text{Cl}_2$ ,  
 Sulphur dichloride,  $\text{SCl}_2$ ,  
 Sulphur tetrachloride,  $\text{SCl}_4$ ,  
 Sulphur monobromide,  $\text{S}_2\text{Br}_2$ .

Others have been reported but are more doubtful. No compounds of iodine and sulphur are definitely known, although a solid prepared by the evaporation of a mixed solution of iodine and sulphur in carbon disulphide is prepared and sold under the name of sulphur iodide. This is believed, however, to be either an ordinary mixture or at least a solid solution.

### Sulphur Hexafluoride, $\text{SF}_6$

Sulphur hexafluoride was obtained by Moissan by the direct action of fluorine on sulphur. It is a colourless, odourless gas, which is comparatively stable and chemically inert. This latter property is particularly exemplified by the fact that it is unaffected by water, whereas the other halides of sulphur are decomposed by water. In this respect sulphur hexafluoride resembles carbon tetrachloride (page 407), and, with it, differs from most other non-metallic halides.

Now that fluorine can be made on a commercial scale (cf. page 523) the use of sulphur hexafluoride as an insulator in high-voltage electrical and X-ray work is being developed.

**Sulphur decafluoride,  $\text{S}_2\text{F}_{10}$ ,** is reported to have been obtained by the fractionation of the crude hexafluoride (Denbigh and Whytlaw Gray—1934).

**Sulphur monofluoride,  $\text{S}_2\text{F}_2$ ,** is a gas which is obtained by the action of silver fluoride on molten sulphur. It reacts with water forming sulphur dioxide, hydrogen fluoride and free sulphur.

### Sulphur Monochloride, $\text{S}_2\text{Cl}_2$

When dry chlorine is passed into sulphur heated in a retort, Fig. 24.19, the two elements combine directly, forming sulphur chloride— $\text{S}_2\text{Cl}_2$ —

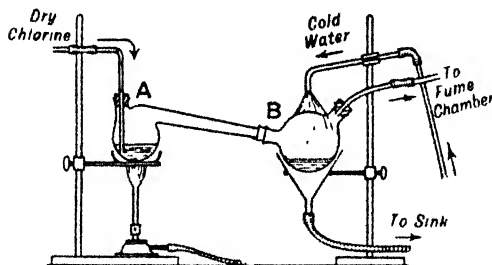
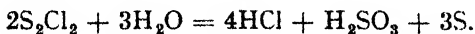


FIG. 24.19.—Preparation of Sulphur Monochloride

which collects in the receiver cooled by a current of cold water, as a yellow liquid. The oil is purified by redistillation. The pale yellow liquid when pure has a pungent smell. It boils between  $138^\circ$  and  $140^\circ$ . The liquid fumes in moist air and is decomposed by water, forming sulphur dioxide, hydrochloric acid, and sulphur:



Sulphur chloride is used as a solvent for sulphur in the manufacture of rubber goods; for decomposing some minerals in analysis; and in preparing some anhydrous chlorides. Its vapour density is 67.5 ( $\text{H}_2 = 1$ ), corresponding with the molecule  $\text{S}_2\text{Cl}_2$ , not  $\text{SCl}$ . Hence "sulphur monochloride" does not appear a very appropriate name for this compound. Its structure has been shown, by electron diffraction,

to be  $\text{Cl}-\text{S}-\text{S}-\text{Cl}$ ; the angles between the two sulphur atoms and the sulphur and chlorine atoms is  $105^\circ$ .

#### Sulphur Dichloride, $\text{SCl}_2$

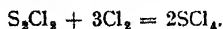
If chlorine be passed into sulphur monochloride, cooled in ice, a garnet-red liquid, said to be sulphur dichloride, is obtained:



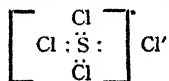
A mixture of liquid chlorine and sulphur monochloride gradually passes into the same product when kept in a sealed tube at  $15^\circ$ . On heating, it decomposes into sulphur monochloride and chlorine.

#### Sulphur Tetrachloride, $\text{SCl}_4$

Sulphur tetrachloride is formed by the prolonged action of chlorine on sulphur monochloride at a temperature below  $-30^\circ$ :



It is a red liquid, with a melting point  $-31^\circ$  and is only stable in the liquid state and in contact with chlorine under pressure. It is now formulated



that is, as a polar compound.

**Sulphur monobromide,  $\text{S}_2\text{Br}_2$ ,** is a red liquid which is formed by dissolving sulphur in bromine, or by heating bromine with sulphur. It resembles sulphur monochloride in behaviour.



## CHAPTER 25

# THE HALOGENS

### § 1 The Halogen Group of Elements

THE elements fluorine, chlorine, bromine, and iodine comprise Group VII<sub>B</sub> of the Periodic Table (page 125) and they form one of the best defined families of elements. They are often referred to as **the halogens**, a name given to them by J. J. Berzelius—from the Greek *ἅλς* (*hals*), sea salt, and *γενναω* (*gennao*), I produce—since these elements (and in particular chlorine, bromine and iodine) are found in sea-water as salts, resembling sea salt, which is sodium chloride. The gradation of properties of these elements, and their compounds, is further discussed at the end of this chapter (page 576).

### § 2 Fluorine

#### Occurrence

Fluorine does not occur free in nature. There is, however, a case recorded by H. Moissan where free fluorine occurs as an inclusion in crystals of fluorspar from Quincié. The compounds of fluorine are widely distributed, though not abundantly, in such minerals as cryolite ( $\text{Na}_3\text{AlF}_6$ ), fluorspar ( $\text{CaF}_2$ ) and fluoapatite,  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{Ca}(\text{ClF})$ , and small quantities occur in some of the micas. It is also said to occur in all rocks, thermal waters, and vapours coming from beneath the earth's crust. Traces occur in sea-water, some mineral springs, bones, teeth, blood, milk, plants, etc. The brain of man has about 3 mgm., and some physiologists believe that the presence of fluorine is necessary in some subtle way, in order that the animal organism can assimilate phosphorus. It has been estimated that the total abundance of fluorine on the earth is comparable with that of carbon, nitrogen and chlorine.

#### History

The fact that glass is attacked when exposed to the fumes produced when fluorspar is warmed with sulphuric acid was known to Schwankhard in 1670, and in 1771 K. W. Scheele stated that fluorspar is the calcium salt of "a peculiar acid"—*fluoric acid*. He prepared this acid by heating fluorspar with sulphuric acid in a tin retort. J. L. Gay-Lussac and J. Thenard (1807) prepared anhydrous hydrogen fluoride, and, following Lavoisier's school, considered fluoric acid to be a compound of water with the oxide of a new element—"fluorium." In 1810 A. Ampère wrote to H. Davy suggesting "many ingenious and original arguments" in favour of the analogy between hydrochloric and hydrofluoric acids. Ampère concluded that hydrofluoric acid

contained no oxygen. The close analogies between calcium iodide, bromide, chloride, and fluoride suggested to A. Ampère that fluorspar is a compound of calcium with an unknown element belonging to the same family as chlorine, bromine, and iodine. Ampère's ideas about hydrofluoric acid were established by H. Davy's experimental work, 1813, and the unknown element was named "fluorine" by analogy with chlorine.

### Preparation

For many years the isolation of fluorine was one of the major problems of chemistry. No one doubted the existence of fluorine, although it successfully withstood every attempted method of isolation, and for over seventy years had never been seen or handled. Fluorine appeared to be so very powerful that no vessel seemed to be capable of resisting its chemical action; and it was compared with the *alkahest* or the universal solvent of alchemy.

All kinds of expedients were tried without success, among which may be mentioned the electrolysis of hydrofluoric acid (Davy), which failed on account of the presence of water (see below); the electrolysis of *anhydrous* hydrogen fluoride which was attempted by Gore, who found it to be a non-conductor; and the action of chlorine on mercuric fluoride in fluorspar vessels (G. J. and T. Knox, 1836). The problem was finally solved by Moissan in 1886 by the electrolysis of a solution of potassium fluoride in anhydrous hydrogen fluoride.

When aqueous hydrofluoric acid is electrolysed, water alone is decomposed, for oxygen is liberated at the anode, and hydrogen at the cathode. The anhydrous acid does not conduct electricity, and it cannot therefore be electrolysed. Moissan found that if potassium fluoride be dissolved in the liquid hydrogen fluoride, the solution conducts electricity, and when electrolysed, hydrogen is evolved at the cathode and fluorine at the anode.

The electrolysis was first conducted in a U-tube made from an alloy of platinum and iridium which is less attacked by fluorine than platinum alone. Later experiments showed that a tube of copper could be employed. The copper is attacked by the fluorine, forming a surface crust of copper fluoride which protects the tube from further action.

In Moissan's apparatus electrodes of platinum iridium alloy were used and the open ends of the tube were closed with fluorspar stoppers, the joints being made tight with lead washers and shellac. During electrolysis the apparatus was immersed in a bath of evaporating methyl chloride.

Moissan's method was very inefficient and was replaced from 1919 onwards by improved processes employing first fused potassium hydrogen fluoride (at 270°) and later by so-called medium-temperature cells working at 80°–85° and using an electrolyte of composition corresponding to  $\text{KF} \cdot 2\text{HF}$ . A convenient form of the first process was that devised

by Dennis, Veeder and Rochow (1931). In their method (illustrated in Fig. 25.1) fused, perfectly dry potassium hydrogen fluoride is electrolysed between graphite electrodes, in a heavy V-shaped tube *A* made of copper, two inches in diameter. The ends are closed with copper caps *B* into which the electrodes *R* are fixed with bakelite cement, which was found to be able to withstand the action of fluorine. The whole cell is lagged with asbestos *H* and heated electrically to fuse the potassium hydrogen fluoride. The fluorine evolved is freed from hydrogen fluoride vapour by passing it through U-tubes *F* and *G* filled with sodium fluoride, with which the hydrogen fluoride forms sodium hydrogen fluoride.

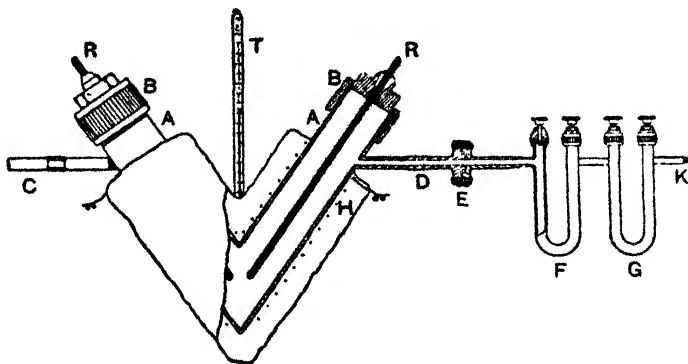


FIG. 25.1—Preparation of Fluorine  
(By permission of the American Chemical Society)

The manufacture of fluorine on a large scale received great impetus from the decision, during the 1939–45 war, to produce an “atomic bomb” by the separation of uranium-235 from natural uranium. This was finally achieved by the diffusion of uranium hexafluoride, on a very great scale, at Oakridge, California. This required the production of fluorine on an industrial scale and cells using the medium-temperature method are now in regular operation. They have anodes of a special non-graphitic form of carbon and cathodes of steel. One such cell is illustrated in Plate 17.

The development of special valves, made of monel metal or nickel with teflon packing, and the use of steel tubing have made fluorine a practicable commercial material. The very low critical temperature of fluorine ( $-129^{\circ}$ ) means that liquid fluorine cannot be transported in cylinders but the compressed gas can be stored at a pressure of 400 lb. per sq. in.

### Properties

Fluorine is a light canary-yellow gas which condenses to a clear yellow liquid boiling at  $-188^{\circ}$ ; and freezes to a pale yellow solid melting at  $-223^{\circ}$ ; at  $-252^{\circ}$  the solid is colourless. Fluorine is

probably the most active element known. It combines with hydrogen with explosion, even in the dark, and at low temperatures, say,  $-210^{\circ}$ . It decomposes water, forming hydrogen fluoride, and liberates oxygen highly charged with ozone. Sulphur, selenium, and tellurium melt and take fire in the gas, forming a mixture of fluorides. Iodine, bromine, phosphorus, arsenic, and antimony combine with the gas with incandescence; so do crystalline silicon, amorphous boron, powdered charcoal. All metals are acted upon by the gas; some take fire spontaneously—e.g., the metals of the alkalis and alkaline earths; others—e.g., magnesium, aluminium, nickel, and silver—require warming to start the reaction; others again require heating to, say,  $300^{\circ}$ , e.g., gold and platinum. Fluorine also liberates chlorine from sodium chloride and from carbon tetrachloride,  $\text{CCl}_4$ . Liquid fluorine has no action on silicon, phosphorus, sulphur and glass. Fluorine does not react with nitrogen or oxygen, even at the temperature of the electric arc or induction discharge. Palladium and iridium are attacked at about  $500^{\circ}$ , and rhodium scarcely at all.

Glass is not attacked by fluorine, if the gas is *entirely* free from hydrogen fluoride. This latter substance can only be removed adequately by cooling the fluorine in liquid air.

Fluorine is a very powerful oxidizing agent. It decomposes water with evolution of oxygen charged with ozone, and this oxygen is liberated associated with a very large amount of energy. As an example of this, fluorine passed into an aqueous solution of potassium chlorate,  $\text{KClO}_3$ , oxidizes it to the perchlorate,  $\text{KClO}_4$ . Fluorine differs from the other halogens in that it forms stable complex acids and complex salts, e.g., hydrofluoboric acid,  $\text{HBF}_4$ ; hydrofluosilicic acid,  $\text{H}_2\text{SiF}_6$ , and cryolite ( $\text{Na}_3\text{AlF}_6$ ).

Fluorine combines with each of the other halogens forming a variety of interhalogen compounds (see page 574). Its intense activity and the small size of its atom enable many elements to exhibit a higher covalency when in combination with fluorine than they can with any other element (cf.  $\text{SF}_6$  and  $\text{OsF}_6$ ).

The development of methods for the production of fluorine on a commercial scale has led to its use for the production of many fluorine compounds in quantity. Already dichlorodifluoromethane (freon 12), used in refrigeration and air conditioning, and a number of similar substances are available.

Fluorine has also been used on a large scale for the manufacture of uranium hexafluoride for the separation of the isotopes of natural uranium; for the production of sulphur hexafluoride which is used as an insulating gas in high-voltage equipment and to make chlorine trifluoride, a substance almost as reactive as fluorine itself but which, with a boiling point of  $12^{\circ}$ , can be stored, liquid, in cylinders.

Polytetrafluoroethylene ( $\text{CF}_2-\text{CF}_2$ )<sub>n</sub> shows exceptional resistance to solvents and boiling acids (including aqua regia) and it is stable up to a temperature of  $325^{\circ}$ .

### Atomic and Molecular Weight of Fluorine

The combining weight of fluorine has been established by converting calcium fluoride, potassium fluoride, sodium fluoride, etc., into the corresponding sulphates.

The best determinations by these methods resulted in values between 18.97 and 19.14, and the best representative value is taken to be 19.00. Cawood and Patterson (1936) determined the atomic weight of fluorine by the limiting density method from the densities of carbon tetrafluoride and methyl fluoride. Their value for the atomic weight is 18.996. No known volatile compound of fluorine is known to contain less than about 19 parts of fluorine per molecule, and hence this is taken as the atomic weight. The vapour density of fluorine corresponds with the formula  $F_2$ .

### § 3 Hydrogen Fluoride, $H_2F_2$

Hydrofluoric acid—an aqueous solution of hydrogen fluoride—is manufactured by the action of 97 per cent sulphuric acid on calcium fluoride (fluorspar):



The operation is carried out in a cast-iron or steel pot or retort connected to a series of leaden boxes containing water or dilute hydrofluoric acid to absorb the gas from the retorts. The condensers are submerged in water to keep them cool. A by-product, calcium fluosulphonate,  $Ca(FSO_3)_2$ , is also formed and remains in the retort. In recent times modifications have been introduced to render the process continuous and absorption of the gas is effected in a series of lead towers. Commercial hydrofluoric acid is marketed in lead, gutta-percha or wax (cerasine) bottles, since it attacks glass. Alternatively, by condensing the vapour in a strongly cooled empty steel, copper or lead receiver almost anhydrous hydrogen fluoride (containing only 0.1 to 0.2 per cent of water) is obtained and is stored in steel cylinders.

Pure hydrogen fluoride is prepared in the laboratory by distilling pure, dry potassium hydrogen fluoride in a copper or platinum apparatus; the pure acid which distils over is collected in a copper bottle cooled in a freezing mixture:



Copper is not affected by the pure acid; it is, however, attacked by the aqueous solution. Anhydrous hydrogen fluoride can also be obtained by passing dry hydrogen over dry silver fluoride.

### Properties

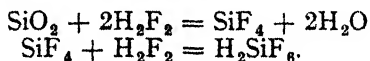
Anhydrous hydrogen fluoride is a limpid liquid which fumes strongly in air. It is very poisonous and dangerous to manipulate. It forms ulcerated sores if a drop comes in contact with the skin. The metals

potassium and sodium dissolve in the pure acid, forming the corresponding fluorides and hydrogen. The liquid acid boils at  $19.4^{\circ}$ ; it does not freeze until cooled to about  $-102^{\circ}$  but the crystals melt at  $-92.3^{\circ}$ . Hydrogen fluoride is very soluble in water, forming a corrosive liquid which readily dissolves many metals with evolution of hydrogen, e.g., iron, silver and copper. If the acid be more concentrated than about 36 per cent, it will become weaker on boiling; and if more dilute, the acid becomes stronger on boiling until an acid containing about 36 per cent of  $\text{H}_2\text{F}_2$ , boiling at  $120^{\circ}$ , is formed. This distils unchanged in composition.

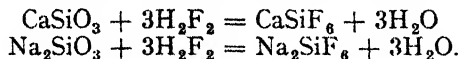
Hydrofluoric acid ( $K = 7.2 \times 10^{-4}$ ) is a weak acid, weaker than phosphoric acid ( $K_1 = 1.1 \times 10^{-3}$ ) but stronger than nitrous acid ( $K = 4 \times 10^{-4}$ ). The anhydrous acid resembles water in certain aspects of its behaviour. Thus, it is associated (cf. page 320 and see below), it has a relatively high boiling point ( $19.4^{\circ}$ ) and it is an ionizing solvent with a high dielectric constant.

The association of hydrogen fluoride is a consequence of the formation of hydrogen bonds (page 320) and is the cause of the abnormally high boiling point.

The action of hydrofluoric acid on silica and silicates in general (e.g., glass) is interesting and important. When a strong solution of the acid is brought in contact with silica, silicon tetrafluoride is formed, which, in presence of excess of hydrofluoric acid, combines with it to form hydrofluosilicic acid:



The action on silicates is similar, for instance with ordinary "soda-glass" (page 779) sodium and calcium fluosilicates are formed:



### Uses of Hydrofluoric Acid

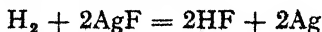
The action of hydrofluoric acid on silica is used for etching glass, e.g., for making the scales on glass instruments. Glass may be etched with the gas or with an aqueous solution of the gas. In the former case, the etching appears opaque and dull; in the latter case, shining and transparent.

Hydrofluoric acid is used for the manufacture of artificial cryolite for use in the aluminium industry (page 743) and it is also employed for freeing artificial graphite (page 362) from silica. In the dyeing industry, double fluorides of antimony and the alkali metals are now used as mordants in place of tartar emetic. In the spirit and brewing industry, hydrofluoric acid is coming into favour as an antiseptic since its effect on yeast is very small compared with its action on other organisms. It is also employed for freeing iron castings from sand, for

removing silica from canes, and has been recommended for cleaning copper. In the laboratory, the solvent action of hydrofluoric acid on silica is made use of in the quantitative analysis of siliceous minerals.

### Composition and Formula of Hydrogen Fluoride

G. Gore (1870) measured the volume of hydrogen necessary to form hydrogen fluoride when heated with silver fluoride at  $100^{\circ}$ , and found that 100 volumes of hydrogen give very nearly 200 volumes of hydrogen fluoride. On the basis of the equation:



this indicates the formula HF at this temperature.

The vapour density at  $26.4^{\circ}$  is 25.59 ( $\text{H}_2 = 1$ ), but, as the temperature is raised, it diminishes steadily until at  $88^{\circ}$  it has fallen to 10.29. This number corresponds with the formula HF. Hence, at lower temperatures, hydrogen fluoride is associated. The effect of hydrogen fluoride on the freezing point of water corresponds also with a molecule  $\text{H}_2\text{F}_2$ , and this is the formula usually adopted, since it is also in agreement with the fact that acid salts (e.g.,  $\text{KHF}_2$ ) are readily obtained. The most probable explanation of the facts mentioned seems to be, however, that the pure liquid (and the vapour at the boiling point) contains molecules in various degrees of association, at least up to  $\text{H}_3\text{F}_3$ ; the concentrated solution consists mostly of  $\text{H}_2\text{F}_2$  molecules; dilute solutions and the vapour above  $88^{\circ}$  are mostly composed of HF molecules.

### Fluorides

The salts of hydrofluoric acid are the fluorides and in many ways resemble the chlorides (q.v.). The principal differences are the formation of acid fluorides (e.g.,  $\text{KHF}_2$ ) and complex salts (e.g.,  $\text{Na}_3\text{AlF}_6$ ), the solubility of silver fluoride and the insolubility of calcium fluoride. (Silver chloride is insoluble and calcium chloride is very soluble.)

### Detection and Determination

In testing for fluorides, the substance under examination is warmed with concentrated sulphuric acid in a leaden vessel covered with a watch-glass. The watch-glass is coated with wax, and a design is scratched on the wax with a pin or knife, so as to expose the glass to the action of the acid. The wax is afterwards removed, and if the design is etched on the glass, fluorides were present.

The standard method for the estimation of fluorides has been to precipitate the fluorine as calcium fluoride, by addition of calcium chloride solution to a solution made from the substance under examination. More recently, however, new methods have been developed in which the fluorine is precipitated as lead chlorofluoride ( $\text{PbClF}$ ), the process having the advantage of greater accuracy over the old method, as well as being applicable either gravimetrically or volumetrically.

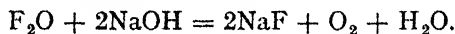
### § 4 Oxygen Compounds of Fluorine

Until 1919, fluorine was believed to be incapable of forming any compound with oxygen, but three oxides,  $F_2O$ ,  $F_2O_2$  and  $FO$ , have now been described and fluorates are also thought to have been made.

(Di)Fluorine monoxide,  $F_2O$ , was obtained by Lebeau and Damiens (1919) by passing a fine stream of fluorine through a 2 per cent solution of sodium hydroxide:



This reaction should be compared with that of chlorine in which sodium hypochlorite and chloride are formed (page 546). The conditions must be so arranged that contact between the oxide and the alkali is as brief as possible since these substances react with the formation of sodium fluoride and oxygen



(Di)fluorine monoxide is a gas with an irritating odour, which does not attack glass and is a powerful oxidizing agent. Unlike chlorine monoxide it does not explode under any conditions. It condenses to a liquid at  $-145^\circ$  and solidifies at  $-224^\circ$ .

Difluorine dioxide,  $F_2O_2$ , is formed by the action of an electric discharge on a mixture of fluorine and oxygen at low pressure and the temperature of liquid air. It is a very unstable red liquid which, when the temperature rises, decomposes into a mixture of fluorine and oxygen and not into  $FO$  as was formerly supposed.

Fluorine nitrate,  $FNO_3$ , has been reported as an explosive gas formed by the action of fluorine on 20 per cent nitric acid at  $0^\circ$ .

### § 5 Chlorine

#### History

Chlorine was first isolated by Scheele in 1774 by the action of manganese dioxide on hydrochloric acid, and was named by him *dephlogisticated marine acid air*. After the overthrow of the phlogiston theory by Lavoisier, it was for a time called *oxymuriatic acid* (muriatic acid being the name by which hydrochloric acid was then known). It was believed to contain oxygen, since Lavoisier had thought that all acids contain oxygen. This view of the nature of chlorine and hydrochloric acid was disproved by Davy in 1810 who demonstrated its elementary nature and suggested the name chlorine—from the Greek *χλωρός* (*chloros*), greenish yellow—on account of its colour.

#### Occurrence

Chlorine does not occur free in nature, but is found in combination in immense quantities. Among naturally occurring chlorine compounds may be mentioned common salt—sodium chloride— $NaCl$ , which is found in the sea and in the form of rock salt, and potassium



chloride (sylvine) and potassium magnesium chloride (carnallite) of the Stassfurt deposits.

The remarkable deposits of potassium, magnesium and sodium salts in the country around Stassfurt, in Prussian Saxony, may be very roughly divided into four strata, illustrated diagrammatically in Fig. 25.2.

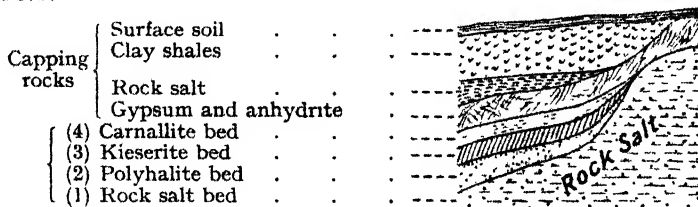


FIG. 25.2 —Diagrammatic Geological Section of a Part of the Stassfurt Salt Bed

(1) *Rock salt bed*.—An immense basal bed of rock salt, broken up at fairly regular intervals with 2 to 5 inch bands of *anhydrite*— $\text{CaSO}_4$ .

(2) *Polyhalite bed*.—Above the basal salt is a layer of rock salt, sometimes 200 feet thick, mixed with bands of magnesium chloride and *polyhalite*— $2\text{CaSO}_4 \cdot \text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

(3) *Kieserite bed*.—Resting on the polyhalite bed is a layer of rock salt, sometimes 100 feet thick, mixed with layers of *kieserite*— $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ —and other sulphates, about 1 foot thickness.

(4) *Carnallite bed*.—Finally comes a reddish layer of rock salt associated with masses of *kainite*— $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; *carnallite*— $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; and a few other salts of magnesium and potassium, e.g., *sylvine*— $\text{KCl}$  and *leonite*— $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ .

These deposits are capped by layers of gypsum— $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ —and anhydrite— $\text{CaSO}_4$ ; rock salt; bunter clay shales; and finally the surface soil. In addition to gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), anhydrite ( $\text{CaSO}_4$ ), and rock salt ( $\text{NaCl}$ ), the principal salts found in the Stassfurt deposits are:

Sylvine . . . . .	KCl
Carnallite . . . . .	$\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Kieserite . . . . .	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Schönite . . . . .	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
Kainite . . . . .	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
Polyhalite . . . . .	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

along with several other salts of lesser importance. These deposits were the subject of extensive investigation by J. A. van't Hoff and his pupils in the light of the Phase Rule (page 185).

It is generally thought that the Stassfurt beds are of marine origin, and have been formed by the natural evaporation of water, during countless years, in an inland prehistoric sea, probably communicating with the ocean by a shallow bar. The sea must have been intermittently replenished by water bringing in more salts, as could occur when

driven over the bar by high tides and gales; there must also have been a number of geological elevations and depressions to account for the succession of strata. The order in which salts are deposited from the evaporation of sea-water is very nearly the same as the geological succession observed at Stassfurt. Neglecting the calcium sulphate, the evaporation of sea-water furnishes successively: (1) a deposit of sodium chloride; (2) sodium chloride mixed with magnesium sulphate; (3) sodium chloride and leonite; (4) sodium chloride, leonite, and potassium chloride, or sodium chloride and kainite; (5) sodium chloride, kieserite, and carnallite; (6) sodium chloride, kieserite, carnallite, magnesium chloride; and (7) the solution dries without further change.

### § 6 Preparation and Manufacture of Chlorine

Chlorine is readily obtained either:

- (i) by oxidation of hydrochloric acid, or
- (ii) by electrolysis of sodium chloride.

The oxidation method was formerly employed almost exclusively, both in the laboratory and industrially, but though still employed in the laboratory it has now given place, to a large extent, to electrolytic processes for the manufacture of chlorine commercially.

#### Laboratory Preparation of Chlorine

For most purposes chlorine is now obtained from a commercial cylinder but, if this is not convenient, chlorine is usually prepared in the laboratory by the oxidation of hydrochloric acid, manganese dioxide or potassium permanganate being the oxidizing agents most often used.

With manganese dioxide, the apparatus indicated in Fig. 25.3 is used.

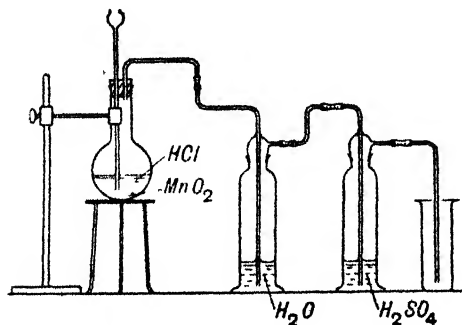
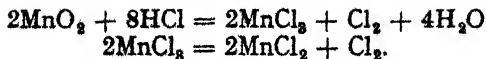


FIG. 25.3.—Preparation of Chlorine using Manganese Dioxide

Manganese dioxide is placed in the flask and concentrated hydrochloric acid, sufficient to cover it, is added through the thistle funnel. The mixture is heated and the chlorine formed is collected by downward delivery, since it is soluble in water. It may previously be passed through a *little* water (to remove hydrogen chloride)

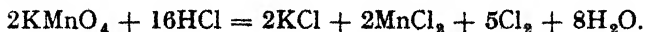
and dried by means of concentrated sulphuric acid. The reaction takes place in two stages, represented by the equations:



The first stage takes place even in the cold, the second only on warming.

A mixture of sodium chloride, manganese dioxide and concentrated sulphuric acid is sometimes used instead of hydrochloric acid and manganese dioxide. Hydrogen chloride is first formed (page 537) and this then reacts as above.

The use of potassium permanganate to oxidize hydrochloric acid is convenient since external heat is not required, and so is often employed. the permanganate being placed in the flask and the concentrated hydrochloric acid added through the tap funnel. The reaction is represented:



Another very convenient laboratory method for the preparation of chlorine is by the action of an acid (usually hydrochloric acid) upon bleaching powder (q.v. page 548).



### Manufacture of Chlorine

Chlorine was formerly manufactured on a large scale by the oxidation of the hydrochloric acid produced in the Leblanc process for the production of sodium carbonate (page 619) but almost the whole of the world's total chlorine output is now made by the electrolysis of brine which produces sodium hydroxide, chlorine and hydrogen at the same time.

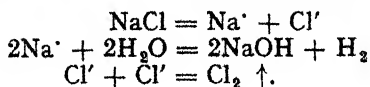
The principal oxidation processes were those associated with the names of Deacon and Weldon, but both have long been obsolete although suggestions have been made for the revival of Deacon's process, in a modified form, for the recovery of chlorine from the hydrogen chloride liberated during the production of organic derivatives of chlorine (cf. page 539).

A variety of catalysts is being tried, some of them consisting of cuprous chloride, as before, along with promoters. Advantage is also being taken of the possibility of using chlorine-resistant materials for the construction of the plant so as to mitigate corrosion problems.

### Electrolytic Processes

The electrolysis of aqueous solutions of common salt produces as final products: an aqueous solution of sodium hydroxide, chlorine and hydrogen, and is now carried out on a very large scale. The chlorine might almost be thought of as a by-product (the hydrogen certainly) since of recent years the demand for caustic soda has increased so much more rapidly than that for chlorine that the disposal of the latter has become a problem.

The actions which take place may be represented:



In practice, it is necessary to devise some method of separating the caustic soda from the sodium chloride and for preventing the sodium hydroxide and chlorine from mixing. Hence the use of special types of cell.

Two main types of cell have been used, viz.:

- (i) cells having a porous diaphragm between the anode and cathode;
- (ii) cells using a mercury "diaphragm" or cathode.

### Porous Diaphragm Cells

A great many cells embodying the porous diaphragm principle have been devised, but for the most part they do not differ in principle. A typical example of such a cell is the **Gibbs cell**, now the most widely used diaphragm cell (Fig. 25.4). In this cell the anodes (a ring of carbon rods) are separated from the cathode (which is a cylinder of iron gauze) by a diaphragm made of asbestos paper. The brine solution, heated to  $85^\circ$ , is introduced continuously in a slow stream into the anode compartment and caustic soda solution drips out from the bottom of the cathode compartment, and is evaporated (see page 616). The chlorine escapes from the top of the anode and is led off through earthenware pipes.

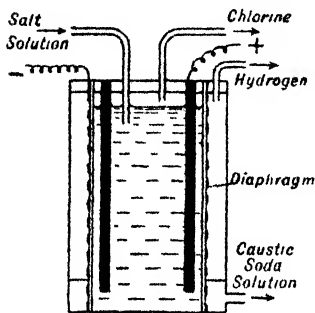


FIG. 25.4.—Gibbs Cell

### Mercury Cells

A cell using a mercury "diaphragm" is the **Kellner-Solvay Cell**, illustrated in Fig. 25.5. It uses graphite anodes and a mercury cathode. A layer of mercury covers the bottom of the cell through which it flows slowly. A solution of sodium chloride flows through the cells. Sodium ions are discharged on the mercury instead of hydrogen ions on account of the high overvoltage of the latter (cf. page 233). The sodium thus dissolves in the mercury, at the cathode, and the chlorine liberated at the anodes escapes via the exit pipes. The sodium amalgam then flows out of the cell into a vessel containing water and there, coming into contact with metallic iron on which hydrogen has only a low overvoltage, is immediately decomposed into sodium hydroxide and mercury, and hydrogen is evolved.

In earlier forms, the cell was given a slow rocking motion by means

of an eccentric so as to make the mercury flow from one compartment to another; but in later types the cell is stationary and the mercury is moved by means of an archimedean screw.

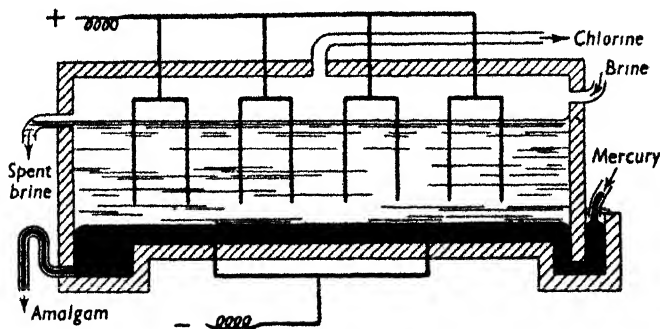


FIG. 25.5 — Kellner-Solvay Cell  
(From Goddard and Hutton, *A School Chemistry for Today*)

The caustic soda solution produced by a mercury cell has a concentration of, at least, 50 per cent and is practically free from salt. That obtained from diaphragm cells is much less concentrated and contains a substantial amount of salt. Very considerable concentration has to be effected, and the salt removed before the product of the diaphragm cell can be marketed. The relative economics of the two processes thus depends on the relation between the cost of fuel and the capital cost of mercury. Rising fuel costs tend to make the diaphragm cell less competitive. At the present time about 75 per cent of electrolytic caustic soda is made in this country by the mercury method.

A further source of industrial chlorine is the process for the manufacture of metallic sodium from fused common salt which has now superseded the Castner process entirely in this country (page 611).

The chlorine manufactured by any of these processes may be used for the preparation of bleaching powder or other chemicals, or it may be liquefied by compression into steel cylinders and sold in this form.

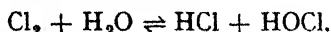
### § 7 Properties of Chlorine

Chlorine is a yellowish-green gas with an irritating and suffocating smell. It attacks the membrane of the throat, lungs and nose and causes serious injury even at high dilutions. It is thus a very poisonous gas. Chlorine is about two and a half times as dense as air and so is the densest of the common elementary gases. It is readily liquefied and forms a dark greenish-yellow liquid which boils at  $-34.1^{\circ}$  at atmospheric pressure. The liquid, contained in steel cylinders (which are not attacked by *dry* chlorine), is an article of commerce. Chlorine melts at

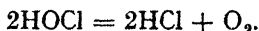
— 101°. Chlorine is soluble in water, 1 volume of water dissolving 4.61 volumes of the gas at 0°, and 2.26 volumes at 20°. It is also soluble in carbon tetrachloride and this solution is used as a reagent.

The solution of chlorine in water, known as **chlorine water**, has the colour, taste and smell of chlorine. If chlorine water be cooled to 0°, yellow octahedral crystals of **chlorine hydrate** separate. Various formulae have been stated for this substance, but it has usually been taken to be  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ . When warmed, chlorine hydrate gives off approximately 100 times its volume of chlorine, and in consequence of this property it was used by Faraday in 1823 for the liquefaction of chlorine (page 46).

The yellow colour of chlorine water gradually disappears on standing, and if exposed to sunlight the solution evolves oxygen. This behaviour is owing to the formation of hypochlorous acid (page 547), through the interaction of the chlorine and water:



Hypochlorous acid decomposes readily in sunlight, forming hydrochloric acid and oxygen:



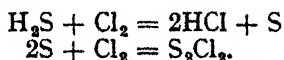
Thoroughly dry chlorine is somewhat inert chemically (cf. page 317), but as ordinarily obtained it is highly reactive. It does not combine directly with oxygen, nitrogen or carbon (although compounds with all three can be obtained indirectly) but with most other non-metals it does so readily. Many, for example, sulphur, phosphorus and arsenic, burn vigorously in chlorine: chlorine forms a number of compounds with the other halogens (page 575).

The interaction of chlorine and hydrogen is particularly interesting, and has been the subject of a great many researches. In sunlight, or when exposed to the light of burning magnesium, equal volumes of hydrogen and chlorine combine with explosion. Yet hydrogen does not appear to combine with chlorine with appreciable velocity in the dark, but in diffused daylight the two slowly combine to form hydrogen chloride. The speed of the reaction is proportional to the intensity of the light. Hence, actinometers have been designed to measure the intensity of light in terms of the speed of combination of a mixture of hydrogen and chlorine gases. If light be filtered through a layer of chlorine gas before it impinges on the mixture of hydrogen and chlorine, the light produces no appreciable effect. Insolated chlorine rises slightly in temperature, even when the heat rays have been filtered from the incident light. It is therefore inferred that *actinic (light) energy absorbed by chlorine is at once degraded into thermal energy. If hydrogen be associated with the chlorine, when exposed to light, the process of degradation of the actinic energy is accompanied by chemical action* (J. W. Mellor, 1902). The presence of minute traces of impurities in the gases retards the rate of combination in a remarkable way.

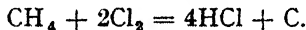
Thus a mixture of fairly pure hydrogen and chlorine, when exposed to diffused daylight, exhibits an *induction period* during which no reaction occurs, and after which the gases begin to react and continue to do so steadily until combination is complete. This induction period has been shown to be caused by the presence of traces of an inhibitor (nitrogen chloride,  $\text{NCl}_3$ , according to D. L. Chapman—1906) which is slowly destroyed by light, so that combination of the hydrogen and chlorine does not take place until the inhibitor has been completely removed.

With the exception of some of the scarcer platinum metals (page 941) all metals are attacked by free chlorine. Many, such as antimony, copper, tin, zinc, magnesium, alkaline earth and alkali metals, burn brightly in the gas; the compound formed being the highest chloride unless this is definitely unstable.

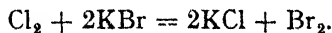
Hydrides of non-metals react with chlorine giving, as a rule, hydrogen chloride, together with either the non-metallic element itself; or a chloride of the non-metal:



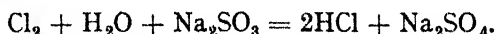
Ammonia yields nitrogen, or nitrogen trichloride according to the conditions (page 442). Hydrocarbons react readily with chlorine; some, e.g., turpentine, inflame spontaneously, carbon being deposited. Others when ignited react similarly, e.g.,



Chlorine readily displaces bromine and iodine from their compounds with metals, e.g.,



Moist chlorine, or chlorine water, is a powerful oxidizing agent. Mention has been made (page 534) of the action of chlorine on water in sunlight, oxygen being given off and hydrogen chloride formed. In presence of an oxidizable substance, this process occurs even in the absence of light. Thus, for example, chlorine oxidizes sulphites in solution to sulphates:



Chlorine may also act as an oxidizing agent more directly. Thus ferrous chloride is oxidized directly to ferric chloride:



and hydrogen sulphide to sulphur



The reaction stops at this stage if the chlorine is dilute (but see above).

On account of its oxidizing properties, moist chlorine will bleach many organic colouring matters. If a piece of coloured litmus paper, or a few coloured flower petals or a piece of cloth dyed with turkey red or indigo, be placed in a jar of dry chlorine, no appreciable change occurs; but if moisture be present, the colours are bleached by the chlorine. This bleaching action of chlorine owing to *oxidation* should be compared with the bleaching action of sulphur dioxide which is caused by *reduction* (page 491) and which therefore is markedly different in character.

### § 8 Uses of Chlorine

The uses of chlorine are many, although the demand for caustic soda (page 618) has increased so much of late that the supply of chlorine available has, at times, tended to exceed the demand.

Chlorine is used extensively in the manufacture of bleaching powder (page 548) and so for bleaching purposes. It is employed in this way for bleaching cellulose fabrics (linen and cotton) which are unaffected by chlorine; nitrogenous fibres (such as silk and wool) are liable to be damaged by it. Chlorine is also used for bleaching wood-pulp and paper. It finds employment in the extraction of gold, the manufacture of bromine, of carbon tetrachloride, sulphur chloride (page 519), chlorinated acetylenes (page 376), carbonyl chloride, and many other organic solvents and chlorine derivatives, and in the dyestuffs industry. It is used in the manufacture of chloroform, and of chlorates (page 550) and hypochlorites (page 547). It is also employed for the sterilization of drinking water, and in swimming baths and for the purification of sewage. It is now also used for "degassing" molten aluminium before casting and is employed in a number of metallurgical processes. An increasing number and variety of compounds, both inorganic and organic, is now made from elementary chlorine. Thus considerable quantities of hydrochloric acid are now manufactured by combining chlorine with hydrogen (page 539).

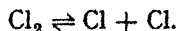
### § 9 Formula and Atomic Weight of Chlorine

The combining weight of chlorine has been determined with very great accuracy by Richards, as indicated on page 105. He obtained the value 35.457. Analysis and determinations of the vapour density of volatile chlorine compounds indicate that these never contain less than about  $35\frac{1}{2}$  parts by weight of chlorine per molecule. Hence the atomic weight is the same as the combining weight. The accepted value at present (1960) is 35.457.

A very careful determination of the density of hydrogen chloride by the limiting density method (page 112) by Gray and Burt in 1909 gave results which lead to the value 35.458 for the atomic weight of chlorine; a value in excellent agreement with that determined chemically.



The vapour density of chlorine below  $600^{\circ}$  is 35.46 ( $H_2 = 1$ ) corresponding with a molecule  $Cl_2$ ; at higher temperatures the density diminishes, showing that partial dissociation into atoms is taking place:



Thus according to Victor Meyer, at  $1400^{\circ}$  the density ( $H_2 = 1$ ) is 29.29, corresponding to a dissociation of about 21 per cent.

### § 10 Detection and Determination of Chlorine

Traces of free chlorine are readily detected by the fact that chlorine liberates iodine from potassium iodide (cf. page 535). Free iodine gives a blue colour with starch—a very sensitive reaction. Hence papers dipped in a mixture of starch solution and potassium iodide solution give a blue colour when exposed to chlorine. (It should be noted that a number of other oxidizing agents will also liberate iodine from potassium iodide.) Chlorine in rather larger quantity is detected by its bleaching action on litmus paper.

Free chlorine is determined by passing it into a solution of potassium iodide, and titrating the iodine so liberated with a standard solution of sodium thiosulphate (page 567).

The detection and determination of chlorine in the form of chlorides is discussed under hydrochloric acid (page 542).

### § 11 Hydrogen Chloride, Hydrochloric Acid, HCl

#### History

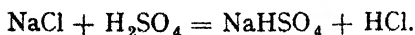
Judging from the writings attributed to Geber, hydrochloric acid was known to the early Arabian chemists; but the preparation of the pure acid—*spiritus salis*—seems to have been first described by the author of the writings ascribed to Basil Valentine (1644). The acid appears to have been made by distilling a mixture of common salt and green vitriol (ferrous sulphate). J. R. Glauber (1648) described the preparation of the acid by the action of sulphuric acid on rock salt. Stephen Hales (1727) noticed that a gas very soluble in water was made by heating sulphuric acid with sal ammoniac (ammonium chloride), and J. Priestley, about 1772, collected the gas over mercury, and gave it the name *marine acid air*. It was later renamed *muratic acid* and, when the elementary nature of chlorine had been established, the name hydrochloric acid was given to it.

#### Preparation and Manufacture

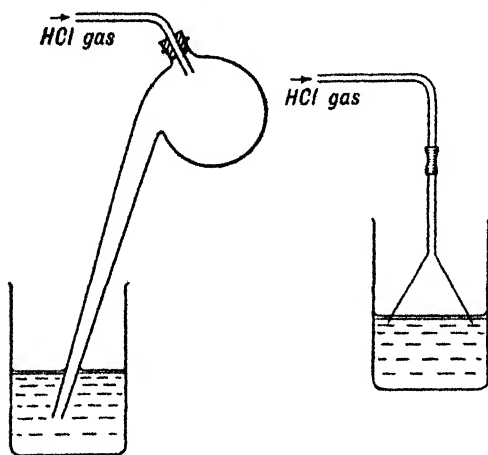
##### Laboratory Preparation

Hydrogen chloride is usually made in the laboratory by the action of concentrated sulphuric acid upon common salt. The experiment is performed by means of apparatus similar to that shown in Fig. 25.3,

the wash-bottle containing water being omitted. Salt is placed in the flask, concentrated sulphuric acid is added through the thistle funnel and the mixture is warmed. Hydrogen chloride is evolved as a gas and may be dried by passing through wash-bottles containing concentrated sulphuric acid. It can be collected by downward delivery as shown in the diagram, or over mercury, but not over water as it is extremely soluble. At temperatures below a red heat, the reaction is represented:



If it is desired to prepare a specimen of the aqueous solution, precautions must be taken when passing the gas into water in order to prevent the liquid from being "sucked back" owing to the high solubility of the gas.



FIGS. 25.6 and 25.7.—Anti-Suck-back Devices

Two methods of doing this are indicated in Figs. 25.6 and 25.7 and are self-explanatory. These methods can be employed in the preparation of solutions of highly soluble gases, in general.

It is often convenient in the laboratory, when the gas is required, to prepare it from the commercial solution. This can easily be done by adding concentrated sulphuric acid by means of a tap-funnel to a quantity of the solution (ordinary concentrated hydrochloric acid) contained in a flask fitted with a delivery tube.

### Manufacture

Hydrochloric acid is manufactured as a by-product of the production of sodium sulphate from sulphuric acid and common salt (page 629).

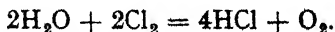
The hydrogen chloride is led off, cooled and absorbed in water either by passing up a tower filled with coke down which water is trickling, or by means of special counter-current absorption plant.

Hydrochloric acid and sodium sulphate are also made from salt and sulphur dioxide by **Hargreave's Process**. In this process salt is heated to 500° in a stream of sulphur dioxide (from pyrites burners, etc.) mixed with excess of air and some steam. Under these conditions, sodium sulphite and hydrogen chloride are formed, the former being

then oxidized to sulphate by the oxygen of the air. The final result is represented:



Hydrochloric acid is now made in increasing quantities by direct combination of the hydrogen and chlorine obtained as by-products in the manufacture of electrolytic caustic soda (page 533). The combination is effected by burning chlorine in large vertical silica tubes or by passing a mixture of chlorine and steam over a catalyst consisting of active charcoal:

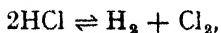


The hydrogen chloride produced is very much purer than that made by the older processes, and is absorbed in water by similar methods.

Considerable quantities of hydrogen chloride are also produced as the result of the chlorination of organic compounds on an industrial scale.

### § 12 Properties of Hydrogen Chloride

Hydrogen chloride is a colourless gas which attacks the mucous membrane when inhaled. It forms dense fumes in moist air on account of the fact that a solution of the gas is less volatile than water. In consequence, a mixture of water vapour and hydrogen chloride condenses to droplets of hydrochloric acid. The gas is denser than air, having a vapour density of 18.23 ( $\text{H}_2 = 1$ ). It is extremely soluble in water: 1 volume of water will dissolve 507 volumes of the gas at  $0^\circ$  and 442 volumes at  $20^\circ$ . In consequence of this high solubility, the "fountain experiment" described on page 431 can be performed with hydrogen chloride in place of ammonia. Hydrogen chloride is easily condensed to a liquid by pressure, and the liquid so formed boils at  $-83.7^\circ$  at 760 mm. It freezes to a white solid which melts at  $-112^\circ$ . The gas is stable at temperatures up to  $1500^\circ \text{C.}$ , after which dissociation occurs.



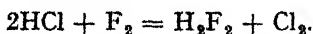
but is only slight at first, being only 0.8 per cent at  $2000^\circ$ .

Aqueous solutions of hydrochloric acid form a constant boiling mixture, containing 20.24 per cent of hydrogen chloride, which boils at  $110^\circ$ . Similar behaviour is observed with nitric acid (page 449) and several other acids.

It was once thought that these constant boiling acids consist of definite compounds of the acids and water, but since the composition of the constant boiling acid varies with the pressure, and since compounds do not vary in composition with changes of pressure, this is clearly not the case.

Hydrogen chloride does not burn and is a non-supporter of combustion. It reacts with free oxygen only in presence of catalysts, such as the copper salts used in the, now obsolete, Deacon process, when

chlorine and water are formed. It reacts with fluorine, which displaces the chlorine, forming hydrogen fluoride:



It does not react with other non-metallic elements.

Its behaviour with metals is such as would be expected of a strong acid. The gas attacks them when heated, and the aqueous solution reacts readily, usually in the cold. Mercury, silver and gold, and the platinum metals are not attacked by hydrochloric acid, and copper only reacts in presence of air or oxygen, but all other metals react forming the chloride and hydrogen, e.g.,



If more than one chloride exists (e.g., iron) the lower chloride usually results.

The aqueous solution of hydrogen chloride (known as hydrochloric acid) exhibits the properties of a strong acid, reacting with oxides and hydroxides of metals to form salts (chlorides) and displacing weak acids from their salts.

Oxidizing agents, as already mentioned (page 530), oxidize hydrochloric acid to chlorine; e.g., peroxides, lead dioxide, dichromates, and permanganates all act upon it in this way.

Nitric acid will also oxidize hydrochloric acid, and this example has an interest of its own since a mixture of concentrated nitric and hydrochloric acids, in the proportions of one volume of the former to three or four of the latter, will dissolve gold and platinum and hence is known as **aqua regia**—the kingly water. This name was given to it by the alchemists because it dissolves the very king of metals, gold. The mixture becomes coloured at about 10° and evolves gas at about 30°; the action is vigorous at 90°, and at 109° a mixture of nitric and hydrochloric acid distils over. The greater oxidizing and solvent properties of aqua regia as compared with nitric acid, etc., are generally attributed to the presence of free chlorine, the reaction being represented by the equation:



corresponding with the fact that some nitrosyl chloride—NOCl—is also formed. The action is, however, probably more complex than this.

### § 13 Uses of Hydrochloric Acid

Hydrochloric acid is used in the dyestuffs industry and for many minor industrial purposes. Dilute hydrochloric acid is largely used for purifying coke, iron ores and clay, and for regenerating the activity of exhausted animal charcoal, and for "pickling" sheet iron in the galvanizing and tinplate industries. It is employed in the manufacture of a number of chlorides, and in making pottery. It is an important

analytical reagent and, in the form of aqua regia, is used in making gold chloride which is used in photography and in pharmacy.

### § 14 Composition and Formula of Hydrogen Chloride

The composition of hydrogen chloride by volume has been found by decomposing a measured volume of the gas with sodium amalgam in an apparatus such as that indicated in Fig. 25.8.

The closed limb of the U-tube is filled with dry hydrogen chloride at atmospheric pressure as far as the lower stopcock, the apparatus having been filled previously with dry mercury which is run out through the tap as the gas enters. The stopcocks are then closed and the remaining mercury replaced by liquid sodium amalgam. The lower stopcock is then opened and the gas brought in contact with the amalgam which decomposes it on standing, forming sodium chloride and hydrogen. The volume of gas remaining, after levelling, is found to be half that of the hydrogen chloride taken. Thus, hydrogen chloride contains half its volume of hydrogen.

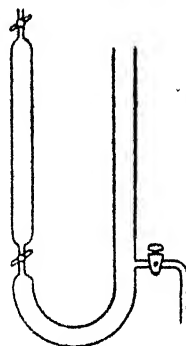


FIG. 25.8.—Volume Composition of Hydrogen Chloride

The composition can be determined also by synthesis, for which purpose the apparatus, Fig. 25.9, is used.



FIG. 25.9 — Combination of Hydrogen and Chlorine

One bulb is filled at atmospheric pressure with hydrogen and the other with chlorine, the bulbs being equal in volume. The apparatus is exposed to diffused daylight and the centre tap opened so as to allow the gases to mix. After some hours the greenish colour of the chlorine will have disappeared, and if one of the end taps be opened under mercury it will be found that no change of volume has occurred. On opening under dilute potassium iodide solution similarly the solution will completely fill the apparatus and no iodine will be liberated. In this way it is shown that hydrogen chloride has been formed, and that no chlorine or hydrogen remains uncombined.

These experiments show that one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride. This result is quoted in Chapter 5 as evidence that the hydrogen molecule must contain *at least* two atoms. If hydrogen chloride can be shown to be  $\text{HCl}$  and not  $\text{H}_n\text{Cl}_n$ , then the hydrogen molecule is  $\text{H}_2$ .

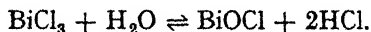
Hydrogen chloride is an acid in solution and hence, in common with all acids, contains hydrogen replaceable by metals. Acids differ from each other in the number of stages by which this hydrogen can be displaced (cf. page 342). Some, such as orthophosphoric acid, can have the hydrogen displaced in *three* stages, so forming three series of salts. Others, like sulphuric acid, form *two* series of salts; whilst from many others the hydrogen can only be displaced in one step.

If hydrochloric acid had the formula  $H_nCl_n$ , we should expect to be able to displace the hydrogen in  $n$  stages. In fact, it can only be removed in one stage—i.e., all the hydrogen or none is displaced and only one series of chlorides is found. Hence it is inferred that the formula for hydrogen chloride is HCl.

### § 15 Chlorides

The salts of hydrochloric acid, the chlorides, will be found described in the chapters devoted to the metals concerned.

They are mostly well-crystallized compounds which are readily soluble in water. Lead chloride and palladous chloride are only very sparingly soluble, and mercurous, cuprous, silver, thallous and aurous chlorides are virtually insoluble. They are not, as a rule, decomposed by heat (gold and platinum chlorides are the only exceptions) and are relatively stable towards water, although some, such as the chlorides of antimony and bismuth, and elements, known as metalloids, which exhibit only feeble metallic properties, give oxychlorides with water, e.g.:



This behaviour is related to the strength of the base concerned. The chlorides of strong bases are not hydrolysed in aqueous solution; those of weak bases are largely hydrolysed. (Cf. page 269.)

#### Detection and Determination

Chlorides are detected in solution by the formation of a white precipitate of silver chloride on addition of silver nitrate solution to a solution acidified with nitric acid. This precipitate is soluble in dilute aqueous ammonia, but is reprecipitated on acidifying with dilute nitric acid, and turns violet in light.

A convenient method for the detection of chlorides in the solid state is to heat a small quantity, mixed with manganese dioxide, with concentrated sulphuric acid. If a chloride is present, chlorine will be evolved. Further confirmation can be obtained by mixing a sample of the substance with potassium dichromate and concentrated sulphuric acid and warming when red vapours of chromyl chloride (page 872) are evolved which condense in blood-red drops on the cooler parts of the tube.

The reaction with silver nitrate serves for the determination of

chlorides both gravimetrically and volumetrically; in the former case, the chlorine is weighed as silver chloride; in the latter, the volume of a standard silver nitrate solution required for the complete precipitation of the chloride present in a known volume of solution is determined.

### § 16 Oxides of Chlorine

Chlorine forms three well-known oxides, viz.:

Chlorine monoxide,  $\text{Cl}_2\text{O}$ ,  
 Chlorine dioxide or peroxide,  $\text{ClO}_2$ ,  
 Chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ .

Two other oxides have also been described:

Chlorine hexoxide,  $\text{Cl}_2\text{O}_6$ ,  
 and Chlorine tetroxide  $(\text{ClO}_4)_x$ ,

but the latter especially is doubtful.

#### Chlorine Monoxide, $\text{Cl}_2\text{O}$

Chlorine monoxide is made by passing dry chlorine over precipitated mercuric oxide (which has been previously heated to about  $400^\circ$ ). The mercuric oxide is placed in a tube *C* cooled by water as shown in

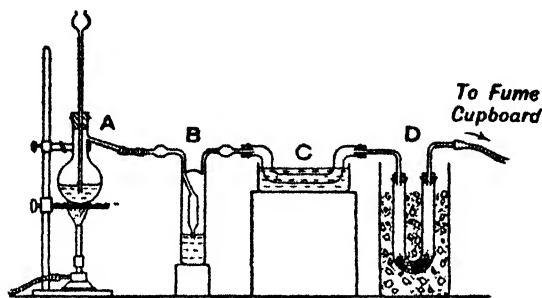
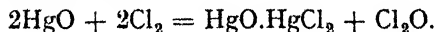


FIG. 25 10.—Preparation of Chlorine Monoxide

Fig. 25.10. Chlorine is generated in the flask *A*, and passed through water in *B* to remove hydrochloric acid.

Chlorine monoxide is formed and is condensed in a U-tube *D* immersed in a freezing mixture:



Chlorine monoxide is a pale orange-yellow gas at ordinary temperatures; it readily condenses to a reddish-brown liquid which boils at  $3.8^\circ$  at 766 mm. Both the liquid and the gas are very unstable, and mere contact with sulphur, phosphorus and many carbon compounds

(e.g., turpentine) leads to decomposition with explosive violence. The liquid is readily exploded by slight mechanical shock, even by pouring from one vessel to another.

Chlorine monoxide dissolves readily in water, one volume of water dissolving 200 volumes of the gas at 0°, and forms hypochlorous acid (page 246):



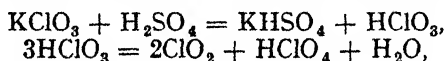
Chlorine monoxide may thus be regarded as hypochlorous anhydride.

The composition of chlorine monoxide is indicated by the fact that when heated (with suitable precautions to prevent explosion) it is decomposed into chlorine and oxygen; and it is found two volumes of chlorine and one volume of oxygen are formed. The vapour density is about 43.5 ( $\text{H}_2 = 1$ ) and hence chlorine monoxide has the formula  $\text{Cl}_2\text{O}$ .

### Chlorine Dioxide, Chlorine Peroxide, $\text{ClO}_2$

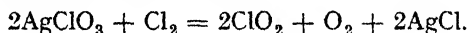
Chlorine dioxide results when concentrated sulphuric acid acts on chlorates. It was discovered in this way by Davy (1815).

The reactions which take place are usually represented:



the chloric acid first formed decomposing into chlorine peroxide and perchloric acid.

It is best prepared by the action of dry chlorine on silver chlorate at 85°–95° (King and Partington, 1926).



It is separated from the oxygen, formed at the same time, by condensing it in a freezing mixture of solid carbon dioxide and ether, when it is obtained as an orange-coloured solid (Fig. 25.11).

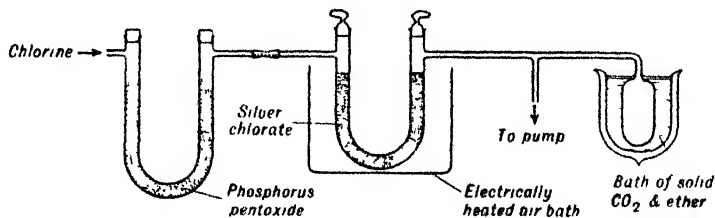
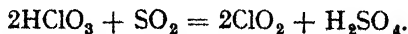


FIG. 25.11.—Preparation of Chlorine Dioxide

Chlorine dioxide is manufactured by passing a mixture of sulphur dioxide and air through a mixture of sodium chlorate and diluted sulphuric acid

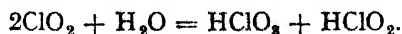




The chlorine dioxide is then converted into sodium chlorite (*vide sub*, page 550) from which it can be recovered for use (e.g., as a bleaching agent for flour) by the action of chlorine. This can be effected by acidification of a suitable mixture of sodium chlorite and hypochlorite solutions



Chlorine peroxide is a reddish-yellow gas with an unpleasant smell. The gas is much denser than air, and is collected by downward delivery, since it decomposes in contact with mercury, and it is fairly soluble in water. Water at 4° dissolves about twenty times its volume of the gas. When the solution is cooled to lower temperatures a crystalline hydrate separates—possibly as  $\text{ClO}_2 \cdot 8\text{H}_2\text{O}$ . On standing, in the dark, an aqueous solution of chlorine peroxide forms a mixture of chloric and chlorous acids.



When the gas is cooled, it condenses to a dark red liquid which boils at 9.9° at 731 mm., and the liquid can be frozen to orange-coloured crystals melting at -59°. Chlorine peroxide is very unstable. It decomposes with explosive violence if an electric spark be passed through the gas, or if a hot wire be introduced into the gas. Chlorine peroxide also decomposes into its elements if it be exposed to the light. The gas is liable to explode suddenly, especially if in the liquid or solid condition, or if organic matter be present. Chlorine peroxide is a powerful oxidizing agent—a piece of phosphorus, sugar, or other combustible takes fire spontaneously in the gas.

The composition of chlorine dioxide was first determined by Davy, and confirmed in 1875 by Pébal, who obtained by decomposition of the gas one volume of chlorine and two volumes of oxygen. This fact, combined with the knowledge that the vapour density is about 33.75, indicates that the formula is  $\text{ClO}_2$ .

**Chlorine heptoxide,  $\text{Cl}_2\text{O}_7$ ,** is obtained by adding perchloric acid (page 554) very slowly to phosphorus pentoxide cooled to -10°, and after standing for a day at this temperature, distilling the mixture at 82°.



It is also obtained by the action of chlorosulphonic acid on potassium perchlorate (F. Meyer, 1921).

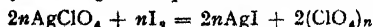
The chlorine heptoxide condenses to a colourless volatile oil (b.p. 82°, m.p. -91.5°) which decomposes in a few days. It is soluble in benzene which it slowly attacks; it also reacts with iodine, slowly in darkness, rapidly in light, forming what is probably *iodine heptoxide*— $\text{I}_2\text{O}_7$ ; but it does not react with bromine. Chlorine heptoxide explodes in contact with a flame, and by sharp percussion. It may be poured on organic matter—paper, wood, etc.—with impunity for the oil simply volatilizes in air. It reacts with water, forming perchloric acid.

Chlorine hexoxide,  $\text{Cl}_2\text{O}_6$ , was discovered by Millon in 1843, but overlooked until in 1925 it was rediscovered by Bodenstein. He obtained it as a red liquid, melting at  $3.5^\circ$  by exposing a mixture of chlorine dioxide and ozone to light.

Its molecular weight in carbon tetrachloride solution corresponds to the formula  $\text{Cl}_4\text{O}_6$ , but its vapour has been found to be paramagnetic, requiring the presence of an odd electron. This would be in accord with the formula  $\text{ClO}_3$ , thus



Chlorine tetroxide  $(\text{ClO}_2)_x$  is said to have been obtained in ethereal solution by Gomberg (1923) by treating silver perchlorate with iodine:



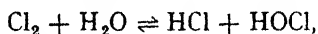
### § 17 Oxyacids of Chlorine

The known oxyacids of chlorine are:

Hypochlorous acid,  $\text{HOCl}$ ,  
Chlorous acid,  $\text{HClO}_2$ ,  
Chloric acid,  $\text{HClO}_3$ ,  
Perchloric acid,  $\text{HClO}_4$ .

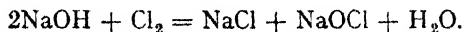
#### Hypochlorous Acid, $\text{HOCl}$

It is probable that a cold aqueous solution of chlorine contains some hypochlorous acid:



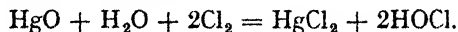
since chlorine water conducts electricity, and some hypochlorous acid can be obtained by distillation of the solution.

A similar reaction occurs between chlorine and cold dilute aqueous alkali, e.g.:



(If the solution is hot, chlorates are formed—page 550.)

Hypochlorous acid can be prepared by shaking freshly prepared chlorine water with mercuric oxide and distilling. A dilute solution of the acid collects in the receiver.



Hypochlorous acid is too weak an acid to react with mercuric oxide in these circumstances.

A convenient way of preparing a solution of hypochlorous acid is by the action of dilute nitric acid or boric acid on bleaching powder (q.v., page 548). The bleaching powder, when dissolved in water, gives a mixture of chloride and hypochlorite.

The latter is decomposed by the nitric (or boric) acid:

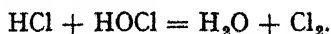


A dilute solution of the acid may be obtained by distillation as before, and may be concentrated further by evaporation in the cold; but

solutions of greater strength than 5 per cent disproportionate on warming into chloric (page 550) and hydrochloric acids:

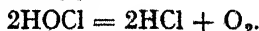


Some chlorine is also evolved by interaction of this hydrochloric acid with unchanged hypochlorous acid:

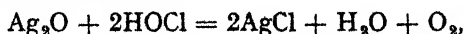


In consequence, pure hypochlorous acid free from water has not been obtained. A solid, crystalline hydrate  $\text{HOCl} \cdot 2\text{H}_2\text{O}$  is known.

When warmed, hypochlorous acid solutions, in addition to the products named above, yield oxygen:



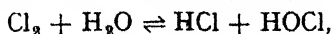
This is particularly the case in sunlight and in presence of oxidizing agents. Thus with silver oxide:



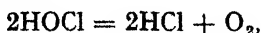
or, if a little cobalt nitrate solution be added to a dilute solution of hypochlorous acid, oxygen is readily evolved on warming—the cobalt ion acting as a catalyst (page 238). This is the basis of the method for preparing oxygen from bleaching powder referred to on page 334. Other metallic ions behave similarly but are usually less effective.

Hypochlorous acid is consequently a powerful oxidizing agent. Thus, if a solution of bleaching powder be boiled for some time with a solution of lead acetate, puce-coloured lead dioxide,  $\text{PbO}_2$ , will be precipitated; and if boiled with a solution of a manganous salt, manganese dioxide,  $\text{MnO}_2$ , will be precipitated. More prolonged boiling may give a green solution of calcium manganate, or a pink-coloured solution of calcium permanganate,  $\text{Ca}(\text{MnO}_4)_2$ .

The rapid decomposition of hypochlorous acid in sunlight renders it probable that the action of light on chlorine water results in the formation of the hypochlorous acid by hydrolysis:



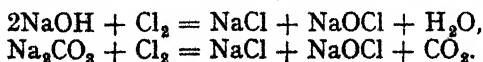
which is at once decomposed:



so that the hydrolysis goes to completion, and leaves, as final products, hydrochloric acid, water and oxygen.

The salts of hypochlorous acid, the hypochlorites, since they are more readily obtained, and more stable, are of greater importance than the acid itself. The principal ones are sodium hypochlorite and bleaching powder.

**Sodium hypochlorite** is obtained in solution by passing chlorine into a cold, dilute solution of sodium hydroxide, or sodium carbonate:



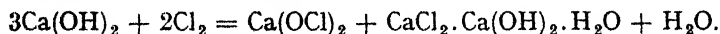
Large amounts of sodium hypochlorite solution are now manufactured by electrolysis of a cold solution of sodium chloride under conditions which result in the mixing of the chlorine and caustic soda first formed.

The salt cannot be obtained free from water as it decomposes on warming, forming the chlorate and chloride (cf. the acid); but by the evaporation at a low temperature of highly concentrated solutions of sodium hydroxide saturated with chlorine, crystals of the composition  $\text{NaOCl} \cdot 6\text{H}_2\text{O}$  (slightly contaminated with sodium chloride) have been obtained.

Sodium hypochlorite, like the parent acid, has a strong bleaching and germicidal action, and is a powerful oxidizing agent.

### Bleaching Powder, Chloride of Lime

Bleaching powder, which is now believed to be a mixture of calcium hypochlorite with a basic calcium chloride (*vide sub*), is made on a large scale by the action of chlorine on slaked lime (quicklime does not react with chlorine at ordinary temperatures):



With very dilute chlorine, such as that which was produced by Deacon's process, it is necessary to ensure very close contact between the gas and the slaked lime, and this is effected by the use of special types of plant, such as that indicated in Fig. 25.12, which illustrates the Hasenclever cylinder apparatus.

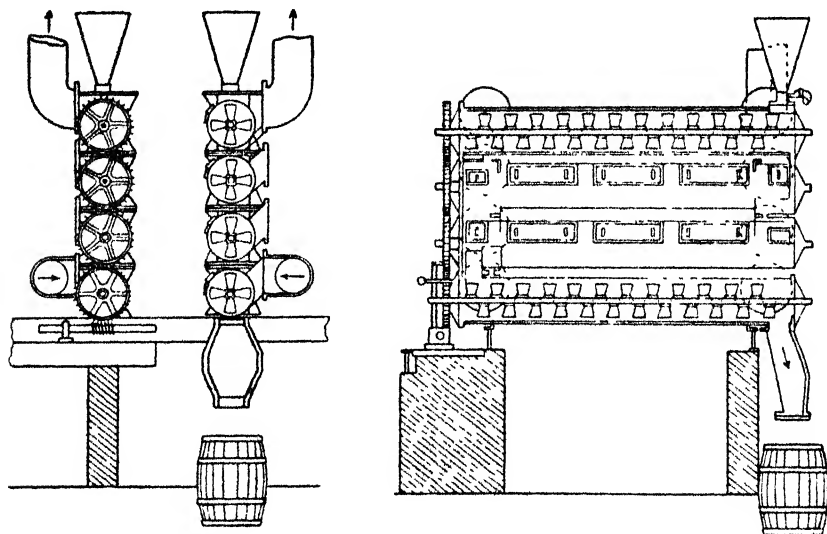


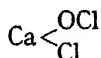
FIG. 25.12 —Manufacture of Bleaching Powder

It consists of six or eight horizontal cast-iron cylinders arranged one above the other, each provided with an archimedean screw which is kept slowly revolving. Slaked lime is fed into the topmost cylinder, after traversing which it passes into the next lower cylinder, and so on. Chlorine is fed in at the bottom and passes through the apparatus in a direction opposite to that of the slaked lime.

In later plant a single large rotating cylinder is used and fed with electrolytic chlorine diluted with air. By careful regulation of the temperature in different parts of the cylinder by means of water cooling, a bleaching powder of high chlorine content, stable in hot climates, can be made.

The amount of chlorine absorbed is never so complete as is represented by the equation quoted above. The commercial value of the bleaching powder depends on the amount of available chlorine it contains. The amount of available chlorine depends upon the method of preparation, temperature, etc.

The constitution of bleaching powder has been much discussed. Under very favourable conditions, slaked lime can be saturated with no more than 43.5 per cent of available chlorine, and the facts correspond with the formula, ascribed to W. Odling, viz.:



and for long accepted.

It has now been shown (Bunn, Clark and Clifford, 1935) by microscopic examination and by X-ray examination of slaked lime during the process of chlorination, that ordinary bleaching powder is a mixture of calcium hypochlorite,  $\text{Ca}(\text{OCl})_2 \cdot 4\text{H}_2\text{O}$  and a non-deliquescent basic chloride,  $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$  in approximately molecular proportions. The first products of the chlorination are this basic chloride and a basic hypochlorite,  $\text{Ca}(\text{OCl})_2 \cdot 2\text{Ca}(\text{OH})_2$ . This latter on further chlorination forms the hypochlorite.

By passing chlorine into milk of lime and evaporating the clear solution *in vacuo* calcium hypochlorite,  $\text{Ca}(\text{OCl})_2 \cdot 4\text{H}_2\text{O}$  is obtained. It is sold commercially under the name *maxochlor* and is said to be more stable than bleaching powder. It is also completely soluble in water and has a high percentage of available chlorine (usually about 74 per cent). *Perchloron* is an anhydrous form of calcium hypochlorite which contains a little slaked lime. The acid is neutralized by the slaked lime present.

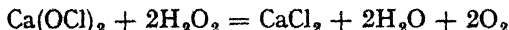
Two methods are in use for the determination of the available chlorine in bleaching powder. In the first the solution or suspension of bleaching powder is treated with excess of potassium iodide solution, acidified with acetic acid and the liberated iodine titrated with sodium thio-sulphate solution.

The second method depends upon the fact that sodium arsenite is oxidized to sodium arsenate by an aqueous solution of bleaching powder.

Excess of a standard solution of sodium arsenite is added to the bleaching powder solution or suspension, and the excess determined by titrating back with a standard iodine solution. The amount of available chlorine is related to the amount of sodium arsenite used as in the equation:



The available chlorine in bleaching powder can also be determined by measuring the volume of oxygen liberated, according to the reaction:



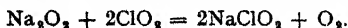
by a known weight of bleaching powder.

### Chlorous Acid, $\text{HClO}_2$ , and Chlorites

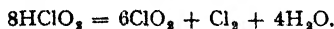
When an aqueous solution of chlorine dioxide is treated with an alkali such as potassium hydroxide, a mixture of potassium chlorite,  $\text{KClO}_2$ , and chlorate is formed:



and if sodium peroxide be employed, sodium chlorite and oxygen result:



Sodium chlorite is now made commercially from chlorine dioxide by passing it into a mixture of sodium hydroxide and hydrogen peroxide solution. The acidified solution probably contains chlorous acid,  $\text{HClO}_2$ . The chlorites are readily decomposed. Lead chlorite,  $\text{Pb}(\text{ClO}_2)_2$ , is precipitated when the solution of sodium chlorite is acidified with acetic acid and treated with lead nitrate. Lead chlorite decomposes with detonation at  $100^\circ$ . The soluble chlorites bleach vegetable colouring matters, even after the addition of arsenious acid. This is not the case with the hypochlorites. Pure chlorous acid has not been prepared; an aqueous solution is obtained by digesting the lead salt with barium carbonate so as to form barium chlorite,  $\text{Ba}(\text{ClO}_2)_2$ , and finally precipitating the barium as sulphate by  $\frac{1}{10}N\text{-H}_2\text{SO}_4$ . The solution gradually decomposes evolving chlorine dioxide and chlorine:



The anhydride corresponding to chlorous acid, which would be chlorine trioxide,  $\text{Cl}_2\text{O}_3$ , is unknown. H. Davy prepared a gas which he called *euchlorine*, and which was at one time believed to be  $\text{Cl}_2\text{O}_3$ , by the action of concentrated hydrochloric acid on potassium chlorate. *Euchlorine* is, however, a mixture of chlorine dioxide and chlorine in varying proportions.

### § 18 Chloric Acid, $\text{HClO}_3$ , and the Chlorates

As mentioned on page 546, when chlorine is passed into a cold solution of potassium hydroxide, a mixture of potassium chloride and hypochlorite is formed; and when the solution of the hypochlorite is boiled, it disproportionates, forming a mixture of potassium chlorate and chloride; otherwise expressed, the hypochlorite solution oxidizes itself:



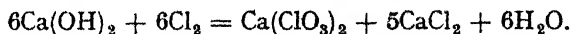
Potassium chlorate is likewise obtained when chlorine is passed into a *hot* ( $70^\circ$ ) concentrated aqueous solution of potassium hydroxide



and the two salts—potassium chloride and potassium chlorate—can be separated by fractional crystallization. Potassium chlorate is far less soluble at room temperature than the corresponding chloride (page 180). C. L. Berthollet (1786–8) first isolated this salt, although it appears to have been known to J. R. Glauber (1658), who mistook it for saltpetre. The above method of preparation is due to J. L. Gay-Lussac (1818).

**Potassium chlorate** can be prepared in the laboratory in this way, but industrially this method is wasteful, since five-sixths of the potassium hydroxide used is converted into potassium chloride, and so a modification due to J. von Liebig (1842) has been used.

A hot suspension of slaked lime in water is substituted for the potassium hydroxide solution, when the reaction may be represented:



The clear solution of calcium chlorate and chloride is concentrated a little by evaporation, and a slight excess of potassium chloride is added. Potassium chlorate has but one-tenth the solubility of the corresponding calcium salt, and is far less soluble than the two chlorides; hence by a further concentration of the solution, the least soluble potassium chlorate separates. The potassium chlorate so obtained is purified by recrystallization.

This old process has now been largely replaced by the electrolytic process. Solutions of potassium chloride of about 25 per cent strength are electrolysed at 70°–75° in iron cells with iron cathodes and graphite anodes under conditions which result in the products being mixed. This is brought about by the use of special types of cell, one of which is indicated in Fig. 25.13:

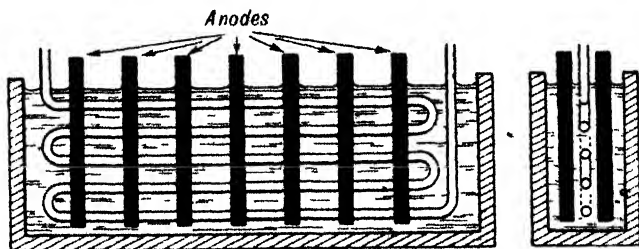
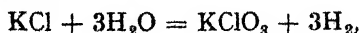


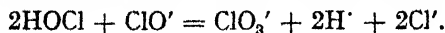
FIG. 25.13.—Chlorate Cell

It consists of an iron tank, containing the potassium chloride solution, in which are immersed a coil of iron pipe and a series of graphite anodes arranged as shown in the diagram. The exposed portions of the tank and the cooling pipe are used as the cathode so that the normal products of electrolysis are formed sufficiently close together to cause reaction

to take place between them. The initial and the end stages of these reactions are represented:



but there has been much difference of opinion about the mechanism of the reaction, the precise nature of which may well differ according to the conditions. The main reaction, however, is now believed to be interaction between hypochlorous acid and hypochlorite ions.



A little potassium chromate or dichromate is often added to prevent reduction of the product by hydrogen at the cathode. The electrolysis is continued until the solution is almost saturated when it is allowed to cool and the potassium chlorate crystallizes out.

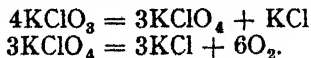
**Sodium chlorate** is manufactured similarly, using saturated common salt solution at 40°. When about two-thirds of the salt has been converted into chlorate, the solution is evaporated. Common salt crystallizes out first and then sodium chlorate.

**Barium chlorate** can be prepared in a similar manner to the above chlorates, either by electrolysis of barium chloride, or by saturating a hot solution of barium hydroxide with chlorine. The separation of barium chlorate and barium chloride is rather difficult because the two salts are almost equally soluble in water.

Barium chlorate is used in the preparation of chloric acid (see below), and in fireworks (green fire).

The chlorates are powerful oxidizing agents. An explosion may occur if a chlorate be mixed with organic matter, charcoal, sulphur, etc., and the mixture struck with a hammer, or heated. Hence mixtures of chlorates with such materials must not be ground together with a pestle and mortar. The materials should be ground separately, and then carefully mixed on paper with a feather. Phosphorus in contact with a chlorate may explode spontaneously. Thus if a drop of a solution of phosphorus in carbon disulphide be allowed to fall on a little potassium chlorate, a loud explosion occurs as soon as the carbon disulphide has evaporated. The oxidizing action of potassium chlorate in neutral or slightly acid solutions is greatly stimulated by traces of osmium tetrachloride,  $\text{OsCl}_4$ , as catalytic agent.

The chlorates are decomposed by heat, with evolution of oxygen, a reaction made use of in the common laboratory preparation of oxygen (page 332). In the absence of a catalyst the reaction takes place in two stages, the perchlorate (page 554) being first formed:



With concentrated sulphuric acid chlorates evolve chlorine dioxide (page 554). The heat of the reaction causes the gas to decompose, which it does with loud crackling. Concentrated hydrochloric acid gives



with a chlorate a mixture of chlorine and chlorine dioxide, known as euchlorine (page 550).

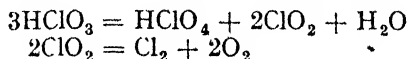
The chlorates are all soluble in water. Potassium chlorate is one of the least soluble of the chlorates. The chlorates are recognized by giving no precipitate with silver nitrate; although, after ignition, the silver nitrate will give a precipitate of silver chloride with an aqueous solution of the residue. If a few drops of a solution of indigo in concentrated sulphuric acid be added to an aqueous solution of a chlorate, and the liquid be acidified with sulphuric acid, and sulphurous acid or a sulphite be added, the chloric acid is reduced to a lower chlorine oxide which bleaches the blue colour of the indigo. If three or four drops of concentrated sulphuric acid be allowed to run down the side of a test-tube containing a little chlorate solution mixed with aniline sulphate, a blue colour appears where the two liquids meet. Nitrates and iodates give a brownish-red coloration under similar circumstances.

Potassium chlorate is used medicinally in throat lozenges. It is employed in the manufacture of matches, fireworks and explosives, as an oxidizing agent and for the preparation of oxygen in the laboratory. Chlorates are also used in calico printing, and in the preparation of dyes. Sodium chlorate is used as a weed-killer and in the manufacture of aniline black.

**Chloric acid,  $\text{HClO}_3$ ,** was first obtained by J. L. Gay-Lussac (1814). His method consists in treating an aqueous solution of barium chlorate with an equivalent quantity of dilute sulphuric acid, when barium sulphate is precipitated and chloric acid remains in solution:



The barium sulphate is filtered off and the filtrate concentrated by evaporation *in vacuo* over concentrated sulphuric acid. Solutions of chloric acid of greater concentration than about 40 per cent cannot be obtained, as stronger solutions decompose into perchloric acid, chlorine, oxygen and water. This decomposition probably takes place in stages:



(see page 554).

### Properties

The concentrated solution of chloric acid so prepared is a colourless, viscid liquid with a pungent smell. It readily decomposes on exposure to light. The solution is stable in darkness provided organic matter be absent. Wood, paper, etc., decompose the acid at once—very often with spontaneous combustion. Blue litmus is first reddened and then bleached by the acid. Even in a dilute solution, chloric acid is a powerful bleaching agent.

The composition of chloric acid was established by J. J. Stas by the analysis of silver chlorate. A known amount of silver chlorate was

reduced to the chloride by means of sulphurous acid. His results show that the ratio of silver chloride to oxygen in the chlorate is as 1 : 3, i.e., the empirical formula is  $\text{AgClO}_3$ . The molecular weight of the free acid has not been determined satisfactorily, but it is inferred that the acid is  $\text{HClO}_3$  from the absence of any acid salts.

### § 19 Perchloric Acid, $\text{HClO}_4$ , and Perchlorates

Perchloric acid is formed when chloric acid is heated or exposed to light (page 553):



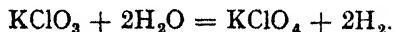
It is prepared by the action of concentrated sulphuric acid on potassium perchlorate:



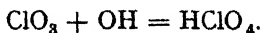
Potassium perchlorate is made, as indicated above (page 552), by the action of heat on potassium chlorate; it is also manufactured electrolytically (see below).

For the preparation of the acid, pure dry potassium perchlorate is mixed with concentrated sulphuric acid and the mixture distilled under reduced pressure. A white crystalline mass of perchloric acid monohydrate,  $\text{HClO}_4 \cdot \text{H}_2\text{O}$ , collects in the receiver. By redistilling this under reduced pressure, pure perchloric acid can be obtained. Aqueous solutions of perchloric acid are also conveniently prepared by the action of fluosilicic acid on potassium perchlorate.

Sodium perchlorate is now manufactured by the electrolysis of the corresponding chlorate with an iron cathode and smooth platinum anode. The over-all reaction is represented



The mechanism is still in doubt; one possible explanation is that chlorate and hydroxyl ions are discharged simultaneously at the anode and then react thus:



Perchloric acid is a volatile colourless fuming liquid; specific gravity 1.764 at 22°, boils at 19° under a pressure of 11 mm., and freezes at -112° to a crystalline solid. If a drop of the acid be brought in contact with paper or wood, instantaneous and violent inflammation occurs; if a drop of the acid be brought in contact with charcoal, a violent explosion occurs. Perchloric acid produces serious wounds in contact with the skin. If the acid be distilled at ordinary pressures, the liquid may gradually become darker and darker in colour, and finally explode violently, especially in presence of even small traces of organic matter or carbon. The pure acid is also said to be liable to darken and to explode after standing some days.

When dropped into water, the two react with a hissing sound, and the evolution of much heat:



Perchloric acid forms five hydrates containing respectively 1, 2, 2.5, 3, and 3.5 molecules of water. The monohydrate is the best known and is formed by adding water to the pure acid until crystals begin to appear. This hydrate melts at  $50^\circ$ , and forms long needle-like crystals. Solutions more concentrated than 71.6 per cent  $\text{HClO}_4$  lose  $\text{HClO}_4$  when distilled, and less concentrated solutions lose water. The "constant boiling acid" contains 71.6 per cent of  $\text{HClO}_4$ , boils at  $203^\circ$ , and distils unchanged in composition. It fumes slightly in air, and may be preserved indefinitely, even in light. Perchloric acid slowly volatilizes at  $138^\circ$  without decomposition.

### Perchlorates

An aqueous solution of perchloric acid reddens litmus, and forms salts—perchlorates—where the radical " $\text{ClO}_4$ " is univalent. Hence perchloric acid is monobasic. It is one of the strongest acids known. While a dilute aqueous solution of perchloric acid reddens litmus, dilute aqueous solutions of chloric and hypochlorous acids bleach litmus. The potassium salt is one of the least soluble perchlorates. It is practically insoluble in absolute alcohol. When perchloric acid is added to an alcoholic solution of a soluble potassium salt, potassium perchlorate is quantitatively precipitated and it is used for the determination of potassium. Unlike the chlorates, the perchlorates are not decomposed by concentrated hydrochloric acid; nor do they yield an explosive gas when warmed with concentrated sulphuric acid. They are not reduced to chlorides by sulphur dioxide; and they require a higher temperature for their decomposition than the corresponding chlorates. Potassium perchlorate in aqueous solution is quantitatively reduced to the chloride when boiled in the presence of neutral ferrous hydroxide and titanous salts. Sodium perchlorate as well as sodium chlorate occur with sodium nitrate in native Chile saltpetre.

Magnesium perchlorate is extremely hygroscopic and has been used as a drying agent under the name *anhydrone*.

The composition of perchloric acid has been found by preparing pure potassium perchlorate from the acid, decomposing a known weight by heating and weighing the potassium chloride remaining. The composition of potassium chloride being accurately known, it is thus possible to determine the ratio of potassium chloride to oxygen. The results indicate that this is as 1 : 4 and hence the empirical formula of the acid is  $\text{HClO}_4$ . It is inferred that this is also the molecular formula since no acid salt of perchloric acid is known.

It has been shown, by X-ray analysis, that the perchlorate ion has the four oxygen atoms symmetrically arranged round the chlorine atom in the form of a tetrahedron.

## § 20 Bromine

### History

Bromine was discovered by A. J. Balard (1826) by the action of chlorine on the residues remaining after crystallization of salt from the water of the salt-marshes of Montpellier. The intensely yellow liquid was extracted with ether, the extract treated with potassium hydroxide, which destroyed the colour, and then evaporated when a white solid was formed. This resembled potassium chloride, but, unlike the chlorides, when heated with manganese dioxide and sulphuric acid it furnished red fumes which condensed to a dark brown liquid with an unpleasant smell. Balard called this substance "muride," but afterwards changed the name to "bromine"—from the Greek *βρωμιος* (*bromos*), stench. Balard demonstrated the elementary nature of bromine, and showed its relation to iodine and chlorine.

J. von Liebig evidently had a sample of bromine in his hands some years previously, but believing it to be iodine chloride (page 575), paid little attention to it.

### Occurrence

Bromine does not occur free in nature. Small quantities occur combined in many silver ores; and it occurs associated with potassium, sodium, magnesium, or calcium in many mineral waters, salt springs, e.g., the Congress and Excelsior springs of Saratoga, Woodhall Spa, and sea-water. The water of the Atlantic is said to contain 0.065 per cent of bromine; the water of the Dead Sea, 4.8 per cent; the mineral water of Ohio, from 3.4 to 3.9 per cent of magnesium bromide.

Bromine is also found in marine animals and plants, in rock salt, human urine, and all commercial products directly or indirectly derived from sea-salt or Stassfurt salts. The saline deposits of Stassfurt contain about 1 per cent of magnesium bromide.

The main supply of the bromine of commerce was formerly drawn from the Stassfurt deposits, and from the saline springs of Ohio and other parts of America; large quantities are now being produced from the salts present in the Dead Sea, and from ordinary sea-water.

It is curious that the Great Salt Lake in Utah, U.S.A., contains practically no bromine.

### Manufacture

The mother liquors remaining after the separation of potassium chloride from the carnallite of the Stassfurt deposits contain about 0.25 per cent of bromine as magnesium bromide. These liquors are allowed to flow down a tower up which a current of chlorine is passing. The chlorine displaces the bromine:



which passes off as a vapour and is condensed in an earthenware coil immersed in water.

An alternative method is by electrolysis of the same mother liquors using carbon electrodes. The magnesium bromide is decomposed before the magnesium chloride, for if any chlorine were formed it would at once decompose the magnesium bromide as just indicated. It is thus possible and practicable to separate the liberated bromine.

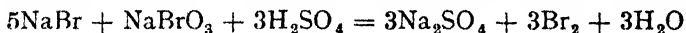
Similar methods are employed in the American and Dead Sea plants.

The bromine is purified by redistillation. The chlorine is removed by distillation from calcium or ferrous bromide, or by collecting separately in a receiver the first 1 to 4 per cent of the distillate in the form of a volatile compound or mixture of chlorine and bromine. If anhydrous bromine be needed, it must be redistilled off concentrated sulphuric acid. If iodide be present, this must be removed by treatment with a copper salt. Cuprous iodide,  $\text{CuI}$ , is precipitated.

The enormously increased demand for bromine in recent years in connection with the motor-fuel industry (see below) led to the initiation of schemes for extracting bromine from sea-water and plant is now in operation at Hayle, in Cornwall, at Amlwch, in Anglesey, as well as at Cape Fear, N. Carolina. The bromine is displaced by chlorine (as in the above methods) after acidification of the sea-water, and is then removed by a current of air. Originally it was absorbed in sodium carbonate solution in towers on the counter-current principle:



The bromide-bromate mixture was acidified with sulphuric acid and



the bromine removed by steam and condensed as in older methods to the liquid.

More recently sulphur dioxide has been used



and the bromine recovered by means of chlorine.

### Properties

At ordinary temperatures, bromine is a dense mobile reddish-brown liquid—specific gravity at  $0^\circ$ , 3.1883. It freezes to a yellowish-brown crystalline mass at  $-7.2^\circ$ , and boils in air at  $58.8^\circ$ . It is very volatile, and gives off a dark reddish-brown vapour at ordinary temperatures. Bromine separates in the form of carmine-red needle-like crystals when a solution of bromine in carbon disulphide is cooled to  $-90^\circ$ . The solid is almost colourless when cooled to  $-252^\circ$ . Bromine has a disagreeable irritating smell, and it attacks the eyes as well as the mucous membrane of the throat and nose. It is poisonous, and attacks the skin, producing troublesome sores. 100 grams of water dissolve

4.3 grams of bromine at 0°, and 3.2 grams at 20°. Bromine is also soluble in chloroform, carbon disulphide, alcohol, ether, and acetic acid. When bromine water is cooled to 0°, it forms **bromine hydrate**,  $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ .

Bromine resembles chlorine in general chemical properties, but is not quite so energetic. It only unites slowly with hydrogen in sunlight, or when heated. It reacts with sulphur, phosphorus, arsenic, tin and other metals in a similar manner to chlorine (page 535), forming the corresponding bromides. Like chlorine, bromine is an oxidizing agent; it differs from chlorine in that it does not react with water, yet if a substance be present capable of undergoing oxidation, hydrogen bromide is formed and the oxygen of the water is available for oxidation. It reacts like chlorine with aqueous solutions of the alkalis, forming hypobromites and bromates. It has bleaching properties similar to those of chlorine, though it is less vigorous as would be expected from its general behaviour.

### Uses

Bromine is used in the chemical industries and, to a large extent, for the production of silver bromide for the manufacture of photographic films, plates and papers. It is also used as a disinfectant, for which purpose it is sold under the name "bromum solidificatum," which is kieselguhr—a siliceous earth—saturated with bromine. Bromine is also used as an oxidizing agent.

It is an important raw material for the manufacture of dyestuffs and of a number of drugs. Of recent years it has been used in large and increasing amount in the preparation of anti-knock motor fuels, of which ethylene dibromide is an important and essential constituent; the lead present in the actual anti-knock constituent (lead tetraethyl) being eliminated from the cylinder as lead bromide. This is now the principal use of bromine.

### Atomic and Molecular Weights

The combining weight of bromine was determined with great accuracy by Richards and Baxter (1906) by the synthesis of silver bromide, and by converting silver chloride into silver bromide. They obtained the value 79.917. Considerations similar to those discussed in connection with chlorine (page 536) indicate that this is also the atomic weight.

A determination of the density, etc., of hydrobromic acid by Moles by the limiting density method leads to the value 79.92. The value accepted by the International Atomic Weight Committee is 79.916.

At about 100° the vapour density of bromine is 84.65 ( $\text{H}_2 = 1$ ), and at 228° it is 79.6, corresponding with the molecule  $\text{Br}_2$ . At 1570° the vapour density is but two-thirds of its value at 228°, showing that the molecule is probably dissociating into atoms.

### Detection and Determination

Free bromine can be detected by the colour of its vapour, formed on warming, provided that it is distinguished from nitrogen peroxide and from chromyl chloride. This may be done by passing the gas into water and shaking the solution with a little carbon disulphide. Bromine, if present, will be extracted by the carbon disulphide which will be coloured orange in consequence. Nitrogen peroxide forms a colourless solution of nitrous and nitric acids; and chromyl chloride gives a yellow solution, the colour of which is not extracted by carbon disulphide.

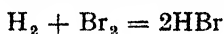
Free bromine is determined volumetrically by making it react with excess of potassium iodide solution, and then titrating the liberated iodine with a standard solution of sodium thiosulphate (page 567).

For the detection and determination of the bromine in hydrobromic acid and bromides, see page 561.

### § 21 Hydrogen Bromide, Hydrobromic Acid, $\text{HBr}$

Hydrogen bromide cannot be prepared by the action of concentrated sulphuric acid on a bromide on account of the ease with which it is oxidized to bromine by sulphuric acid (see below). Phosphoric acid can be used instead of sulphuric acid, but is not commonly employed.

Hydrogen and bromine vapour combine at a red heat, especially in the presence of platinized asbestos, which acts as a catalyst:



and this method can be employed for its preparation in the laboratory.

The most usual method for making the gas is by the action of bromine and red phosphorus on water.

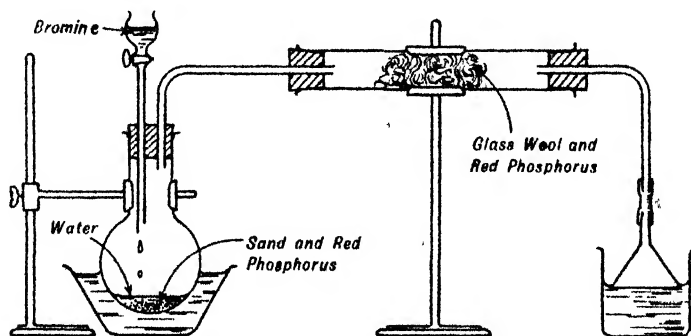


FIG. 25.14.—Preparation of Hydrobromic Acid (using Phosphorus)

The apparatus indicated in Fig. 25.14 is used, consisting of a flask containing a mixture of red phosphorus with twice its weight of water and some clean sand; and fitted with a dropping-funnel containing

bromine. The bromine is allowed to drop slowly on to the phosphorus, when hydrogen bromide is given off and heat is evolved, so that in the initial stages of the reaction it may be necessary to cool the flask in a trough of water. The gas is passed through a tube containing glass wool and damp red phosphorus, to remove any unchanged bromine, after which it may be collected over mercury, or by downward delivery since it is denser than air.

If the solution be required, the gas may be dissolved in water using a funnel, as shown in Fig. 25.14, to prevent the risk of the water being sucked back. Alternatively, two wash-bottles connected as shown in Fig. 25.15 may be used.

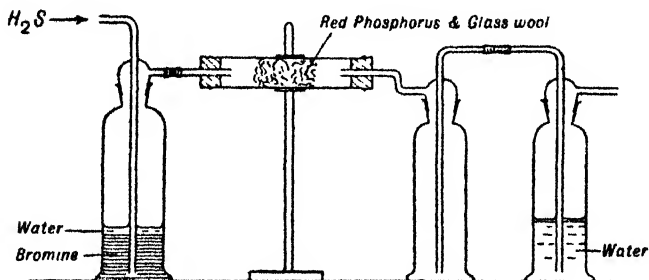
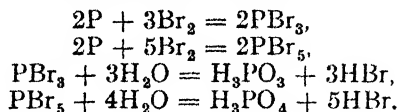


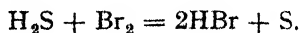
FIG 25.15 - Preparation of Hydrobromic Acid  
(using Hydrogen Sulphide)

The reactions which take place are probably as follows:

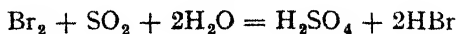


Another convenient method for the preparation of hydrogen bromide is by the action of hydrogen sulphide on bromine, and may be carried out in the apparatus indicated in Fig. 25.15.

A stream of hydrogen sulphide (page 482) is passed through bromine mixed with a little water in a wash-bottle. The hydrogen bromide formed is passed through a tube containing damp red phosphorus as before, and then either collected over mercury, or by downward delivery or dissolved in water by means of two wash-bottles as shown. (Alternatively a funnel may be used as in Fig. 25.14.) The reaction is represented by the equation:



Yet another feasible method is by the action of sulphur dioxide on bromine in presence of a little water. This can be carried out in the



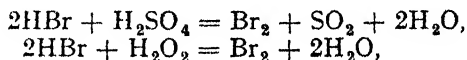


apparatus shown in Fig. 25.15 and gives a very pure product. This is probably the best method for obtaining the aqueous solution.

### Properties

Hydrogen bromide is a colourless gas with a strong penetrating smell. It fumes in air. The gas condenses to a liquid at  $-67^{\circ}$ ; and solidifies to a colourless solid at  $-88.5^{\circ}$ . The gas is very soluble in water. One gram of water at  $0^{\circ}$  dissolves 612 volumes of hydrogen bromide, and 532 volumes at  $25^{\circ}$ . The acid containing 47.63 per cent of hydrogen bromide distils unchanged in composition; weaker acids lose much water, while more concentrated acids lose hydrogen bromide until the constant boiling mixture, which boils at  $124.3^{\circ}$  at 760 mm., is obtained.

Dry hydrogen bromide has no action on litmus. Hydrogen bromide resembles hydrogen chloride very closely in chemical properties, but hydrogen bromide is less energetic. It attacks mercury very slowly, forming hydrogen and mercury bromide. The action is not fast enough to prevent its use in collecting hydrogen bromide. Hydrogen bromide is more easily decomposed than hydrogen chloride; thus at  $800^{\circ}$  the dissociation is appreciable. Slight decomposition also occurs when the gas is exposed to sunlight. Again, it is more readily oxidized than hydrochloric acid; thus sulphuric acid and hydrogen peroxide oxidize it to bromine:



whereas neither of these attacks hydrochloric acid.

### Uses

Hydrobromic acid is an important laboratory reagent, especially in organic chemistry, and it is used for the manufacture of some inorganic bromides.

The **Composition and Formula** of hydrogen bromide have been determined in a similar manner to those of hydrogen chloride (page 541).

### Bromides

Hydrobromic acid forms bromides in the same way as hydrochloric acid forms chlorides, and the two series of salts are very similar. Thus corresponding salts crystallize in the same forms, and closely resemble each other in chemical behaviour, the principal difference being that the bromides are more readily oxidized. Some bromides, e.g., those of potassium and silver, are extensively used in photography, and potassium and sodium bromides are used in medicine.

### Detection and Determination of Bromides

A common method for the detection of bromides is the formation of free bromine when a bromide is warmed with concentrated sulphuric acid and manganese dioxide. The identity of the bromine is established

as indicated on page 559. Another method, available if the salt under investigation is soluble, is to add a few drops of chlorine water to the solution and shake it with a little carbon disulphide. Bromine is liberated and dissolves in the carbon disulphide with an orange colour. Silver nitrate yields an almost white, though slightly cream-coloured, precipitate of silver bromide insoluble in dilute nitric acid and in dilute ammonia, though soluble in concentrated ammonia. It does not turn violet in light as silver chloride does.

Bromides are determined in the same manner as chlorides, making use of their reaction with silver nitrate.

## § 22 Compounds of Bromine and Oxygen

Three oxides of bromine have been described but they are extremely unstable and exist only at very low temperatures, if at all, so that their existence is not universally acknowledged. The preparation of bromine monoxide,  $\text{Br}_2\text{O}$ , and an oxide of the formula  $(\text{Br}_3\text{O}_8)_n$ , has been claimed (Zintl and Reinäker, 1930; Brenschede and Schumacher, 1936). The former is described as a very unstable gas obtained by the action of bromine on specially prepared, very reactive mercuric oxide; or, in solution, by shaking mercuric oxide with a solution of bromine in carbon tetrachloride. The other  $(\text{Br}_3\text{O}_8)_n$  is said to be formed by the action of ozone on bromine vapour at temperatures below  $0^\circ$ , and is also very unstable. Neither of these has received further confirmation. In 1937 the isolation of another oxide of bromine,  $\text{BrO}_3$ , by the action of a glow discharge on a mixture of bromine and oxygen at  $0^\circ$  was reported by Schwartz and Schmeisser.

Two oxy-acids of bromine are definitely known, viz.:

Hypobromous Acid,  $\text{HOBr}$ ,  
Bromic Acid,  $\text{HBrO}_3$ ,

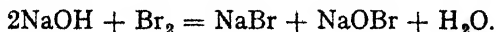
while the existence of

Bromous Acid,  $\text{HBrO}_2$

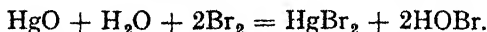
has been reported, but not confirmed. Neither perbromic acid nor any perbromate has hitherto been obtained.

### Hypobromous Acid, $\text{HOBr}$ , and Hypobromites

When bromine is added to a cold aqueous solution of sodium or potassium hydroxide a colourless liquid is obtained which has bleaching properties, and which resembles in many respects a solution of sodium hypochlorite (page 547). Hence it is inferred that the hypobromite has been formed:

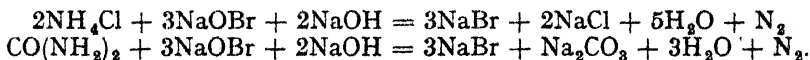


A dilute solution of the corresponding acid can be made by shaking mercuric oxide with a cold aqueous solution of bromine:



The aqueous solution of the acid is unstable and decomposes at  $60^\circ$  into bromine and water, although it can be distilled at  $40^\circ$  under reduced pressure.

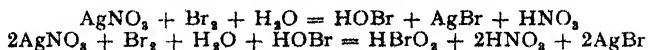
An alkaline solution of sodium hypobromite is used for the estimation of ammonium salts and urea. Nitrogen is evolved quantitatively and its volume serves as a measure of the ammonium salt, or urea, present in the solution:



Hypobromous acid is a very weak acid, much weaker even than hypochlorous acid; its salts, consequently, disproportionate with the formation of bromates more readily than hypochlorites yield chlorates.

#### Bromous Acid, $\text{HBrO}_2$

What is thought to be a solution of bromous acid is formed when an excess of bromine water is shaken with a concentrated solution of silver nitrate. Hypobromous acid is probably first formed, and this is perhaps further oxidized:



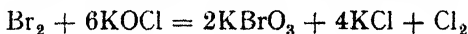
Neither the acid nor its salts have been isolated

#### Bromic Acid, $\text{HBrO}_3$ , and Bromates

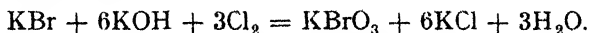
By dropping bromine slowly into a hot, concentrated aqueous solution of potassium hydroxide a yellow solution is formed which soon deposits crystals of **potassium bromate**,  $\text{KBrO}_3$ :



The crystals can be purified by recrystallization from hot water. It is also formed when bromine vapour is passed into a solution of potassium carbonate which has been saturated with chlorine:



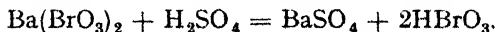
or by passing chlorine into a solution of potassium bromide and potassium hydroxide:



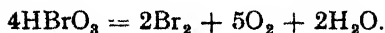
**Barium bromate**,  $\text{Ba}(\text{BrO}_3)_2 \cdot \text{H}_2\text{O}$ , can be prepared similarly from hot barium hydroxide solution and bromine.

The bromates of other metals are obtained by the action of the appropriate carbonate or sulphate on barium bromate.

By treating barium bromate solution with the calculated quantity of sulphuric acid an aqueous solution of bromic acid is obtained:



The solution can be decanted, or filtered, from the precipitated barium sulphate, and concentrated by evaporation under reduced pressure until it contains about 50 per cent of the acid. On further concentration, or on heating, decomposition into bromine, oxygen, and water occurs:



The bromates resemble the chlorates, but there is no sign of the formation of perbromates on heating. Some metallic bromates when heated give the oxide, bromine, and oxygen, e.g.:



### § 23 Iodine

#### History

In 1811, B. Courtois, a manufacturer of saltpetre, near Paris, used an aqueous extract of varec or kelp\* for converting the calcium nitrate from the nitre beds into the potassium salt (page 641). Courtois noticed that the copper vats used for this purpose were rapidly corroded by the liquid, and he traced the effect to a reaction between the copper and an unknown substance in the lye obtained by extracting the varec or kelp with water. On evaporating the aqueous extract of the kelp, crystals of potassium sulphate first separate, then follow crystals of sodium sulphate, sodium chloride, and afterwards sodium carbonate. The remaining liquid when heated with sulphuric acid in a retort furnished "a vapour of a superb violet colour" which condensed in the beak of the retort and in the receiver in the form of brilliant crystalline plates. Courtois communicated his discovery to Clement and Desormes, who published some results of their study of this new substance in 1813. A year later Gay-Lussac published an extensive and remarkable memoir on this new substance which was called iodine—from the Greek *ἰοειδής* (*ioeidēs*), violet. Gay-Lussac established the elementary nature of iodine, and demonstrated its relationship to chlorine. About the same time, H. Davy confirmed many of Gay-Lussac's results.

#### Occurrence

Iodine, although widely distributed, is never found free in nature.

Varec or kelp contains from 0.1 to 0.3 per cent of iodine. The kelp derived from deep seas is richer in iodine than that from shallower parts. Iodine also occurs in small quantities in sea-water; sea plants; sea animals; in some land plants and animals; in cod-liver oil; in the thyroid gland of animals; in many mineral springs and in the salt brine from some petroleum wells. It occurs combined with silver in some Mexican ores, and in some South American lead ores. Most of the iodine of commerce is extracted from the mother liquor remaining after the separation of sodium nitrate from caliche in Chile. Caliche contains about 0.2 per cent of iodine, and the mother liquor, after the extraction of the sodium nitrate, contains 5 to 20 per cent of sodium iodate (page 627).

\* During the stormy months of spring, seaweeds are washed on to the western coasts of Ireland, Scotland, and France. The inhabitants collect the weed and burn it in large heaps at as low a temperature as possible. The ash thus obtained is called *hèlp* in Scotland and *varec* in Normandy.

### Manufacture

Iodine is manufactured:

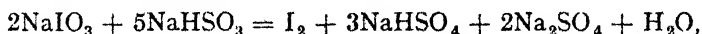
- (i) from caliche, after removal of the sodium nitrate;
- (ii) from seaweed;
- (iii) from salt brine from oil wells in Java and in California.

#### *Iodine from Caliche*

The mother liquor remaining after the crystallization of the sodium nitrate (page 627) is treated with sodium bisulphite solution, which precipitates the iodine.

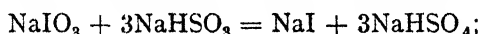
The solid iodine which separates is allowed to settle, washed and pressed into blocks. These are put into cement-lined iron retorts and sublimed into a series of glazed earthenware pipes each about 2 feet in diameter and 4 feet long.

The overall reaction is:

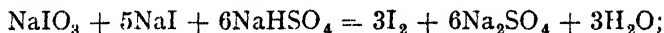


but it probably takes place in stages. These are:

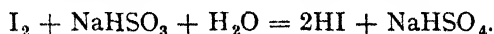
- (i) a slow reaction in which the iodate is reduced to iodide:



- (ii) a fast reaction between iodate and iodide whereby iodine is formed:



- (iii) a very fast reaction, which occurs so long as any sulphite is present, in which iodine is reduced to iodide:



Iodine, therefore, only appears when all the sulphite has been used up; the calculated quantity is consequently used.

#### *Iodine from Seaweed*

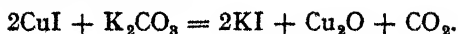
The seaweed is roughly dried and burned, and the fused mass of salts which remains is extracted with water. This aqueous extract is concentrated when potassium sulphate, and chloride, and sodium chloride are deposited.

The mother liquor, which contains iodides and some bromides, is treated with sulphuric acid and manganese dioxide and distilled. Iodine is liberated and condensed in a series of earthenware condensers called "udells."

#### *Iodine from Petroleum Brine*

The Java brine is treated with sulphur dioxide and then allowed to flow over bundles of copper wire suspended in troughs. The iodine is precipitated as cuprous iodide which is filtered off and exported to

Europe. There it is converted into potassium iodide by fusion with anhydrous potassium carbonate.



In California a process has been used in which the iodine was adsorbed on active charcoal from which it is recovered by the action of sodium hydroxide solution. It is now more usual to liberate the iodine with chlorine and recover it with a stream of air.

Iodine is further purified by mixing it with potassium iodide (to remove chlorine and bromine which are usually present in solid solution) and resubliming it.

### Properties

At ordinary temperatures, iodine is a dark bluish-black crystalline solid. The rhombic crystalline plates have a metallic lustre, and a specific gravity of 4.93 at 20°. Solid iodine has a vapour pressure of 0.030 mm. at 0°, rising to 3.084 mm. at 55°; this agrees with the fact that iodine vaporizes slowly at ordinary temperatures, and it has a slight smell resembling chlorine. It is very sparingly soluble in water: 100 ml. of a saturated solution at 25° contain about 0.034 gram of iodine, and is coloured a faint brown. The iodine is much more soluble if potassium iodide be also present.

Iodine is readily soluble in carbon disulphide, chloroform, benzene and other hydrocarbons forming violet solutions; it is also soluble in alcohol, ether, acetone, etc., but in these solvents it forms brown solutions.

It is probable that free iodine is present in the violet solutions; and that the brown coloration is caused by association with the solvent. In brown solutions of iodine in potassium iodide, for example, the iodine is present as an unstable **potassium tri-iodide**,  $\text{KI}_3$ . This salt has indeed been isolated in the form of dark-coloured, needle-shaped crystals.

A great number of **polyiodides** have been prepared, particularly of the alkali metals: e.g.,  $\text{CsI}_5$ ,  $\text{RbI}_3$ ,  $\text{RbICl}_4$ ,  $\text{KI}_3$ , etc.

The tendency of the alkali metals to form polyiodides increases with increasing atomic weight.

Iodine resembles chlorine and bromine in its chemical properties, but it is rather less energetic. Chlorine can displace bromine from bromides, and both chlorine and bromine can displace iodine from iodides. Chlorine can displace bromine from bromates, and iodine appears to displace chlorine from chlorates according to the equation:



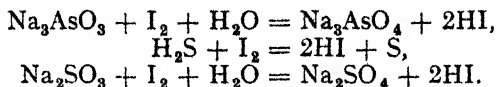
but the reaction is probably not one of simple displacement as is explained on page 571.

Iodine does not combine directly with oxygen, and with hydrogen the reaction is very slow, except in the presence of catalysts (see pages 255, 568).

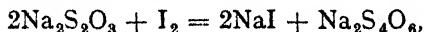
Of the other non-metals only phosphorus, chlorine and fluorine will combine directly with iodine; but most metals react energetically with it, although less so than with the other halogens. Thus antimony powder inflames spontaneously when it is shaken with iodine vapour; iodine and mercury also combine energetically when heated.

When in contact with starch, iodine forms an intense blue coloration. The reaction is delicate enough to reveal the presence of 0.0000001 gram of iodine per ml. The blue colour disappears when heated to about 80°, but returns on cooling. The nature of this blue substance is still uncertain. The most probable explanation is that it consists of iodine adsorbed on colloidal starch particles.

Iodine, like the other halogens, is an oxidizing agent, though much less powerful. It will oxidize, for example, arsenites to arsenates, hydrogen sulphide to sulphur and sulphites to sulphates, reactions which are employed in volumetric analysis in conjunction with a standard solution of sodium thiosulphate:



Iodine in solution reacts quantitatively with sodium thiosulphate, sodium tetrathionate being formed:



and this reaction has many applications in volumetric analysis. It can be employed not only in the determination of iodine itself but for determining the amount of any oxidizing agent which will liberate iodine from an iodide. Examples are chlorine, bromine, cupric salts, hypochlorites, and bleaching powder.

### Uses

Iodine is largely used in medicine, both in the form of the free element (usually in solution in alcohol called "tincture of iodine") and in combination. The tincture is used as antiseptic. Iodine is a constituent also of the antiseptics iodoform ( $\text{CHI}_3$ ) and iodole ( $\text{C}_4\text{I}_4\text{NH}$ ). It is employed in the manufacture of dyes and other organic chemicals, in photography and in analytical chemistry.

### Atomic and Molecular Weights

The combining weight of iodine has been determined by the analysis of silver iodide and other iodine compounds such as iodine pentoxide. The atomic weight is found to be approximately 127 since this is the smallest amount of iodine present in the molecular weight of any known volatile compound. The accepted value for the atomic weight at present (1957) is 126.91.

The vapour density of iodine at 600° is 125.9 ( $\text{H}_2 = 1$ ) which corresponds with a molecule  $\text{I}_2$ . Similarly, the lowering of the freezing

points and raising of the boiling points of solutions of iodine in acetic acid, carbon disulphide and chloroform indicate a molecular weight of approximately 254.

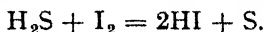
When iodine is heated above  $700^{\circ}$ , the vapour density diminishes steadily up to about  $1700^{\circ}$ , when it becomes constant at about 63.5 indicating dissociation into atoms.

### § 24 Hydrogen Iodide, Hydriodic Acid, HI

Hydrogen iodide, like hydrogen bromide, cannot be made by the action of concentrated sulphuric acid on iodides on account of the ease with which it is oxidized. It is formed by the direct union of hydrogen and iodine, and although the reaction is reversible and incomplete and also slow in the absence of a catalyst (cf. page 255), it can be utilized for its preparation by passing hydrogen and iodine vapour over heated platinized asbestos.

The gas is usually prepared in the laboratory by the action of phosphorus and iodine on water, using the apparatus (Fig. 25.15) employed for the similar preparation of hydrogen bromide. Red phosphorus and iodine are mixed in a dry flask, and a little water is added from a dropping-funnel. (This modified procedure is rendered necessary by the fact that iodine is a solid at ordinary temperatures whereas bromine is a liquid.) Free iodine is removed by passage through a tube containing red phosphorus and glass wool. The gas cannot be collected over mercury as they react; it is usually collected by downward delivery.

The solution in water (known as hydriodic acid) may be prepared by absorbing the gas obtained as described above, in water (using precautions as in the case of hydrobromic acid, etc., to prevent "sucking-back"), but it is often made in the following way. Powdered iodine is suspended in excess of water and hydrogen sulphide is bubbled slowly through the mixture, until the colour of the iodine has disappeared. A rapid stream of carbon dioxide, or hydrogen, is then passed for a short time to remove hydrogen sulphide. The mixture is then shaken to coagulate the free sulphur which is removed by filtration through glass wool. The solution can be concentrated to about 50 per cent by distillation. The reaction is represented:



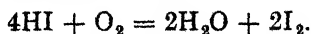
#### Properties

Hydrogen iodide is a colourless gas which fumes strongly in air. It condenses to a colourless liquid at  $0^{\circ}$  under 4 atmospheres pressure. This boils at  $-35.5^{\circ}$ , and freezes to a white solid which melts at  $-50.8^{\circ}$ . The gas is very soluble in water: one volume of water at  $10^{\circ}$  dissolves about 425 volumes of hydrogen iodide. The solution fumes strongly in air, and it has acid properties.

It forms a constant boiling mixture when distilled, containing 57 per cent of hydrogen iodide, which boils at  $127^{\circ}$  at 774 mm.



The solution is colourless, when freshly prepared, but turns brown on keeping owing to formation of free iodine by oxidation:



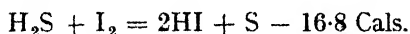
It is a powerful reducing agent on account of the ease with which it is decomposed into hydrogen and iodine and is extensively used for this purpose in organic chemistry. It is also decomposed by exposure to light, and on heating: the following table shows the extent of dissociation at various temperatures.

TABLE XXXIII.—DISSOCIATION OF HYDROGEN IODIDE

Temperature	Per cent. of dissociation
283°	17.9
356°	19.5
444°	22.0
527°	24.7

The dissociation of hydrogen iodide was extensively investigated by Bodenstein (1897), whose values are given in Table XXXIII; the application of the Law of Mass Action to this reaction has been discussed on page 241.

It is interesting to notice that, although hydrogen iodide is formed from *solid* iodine with absorption of heat, its formation from iodine *vapour* takes place with evolution of heat since the heat required to vaporize the iodine is greater than that evolved by the reaction. Consequently the dissociation of hydrogen iodide increases with rise in temperature. Also it may be noted that heat is evolved when hydrogen iodide is prepared in solution from iodine and hydrogen sulphide as described on page 568. This is because although the formation of hydrogen iodide involves absorption of heat



hydrogen iodide evolves 19.2 Cals. per gram molecule when dissolved in water. Consequently the net result of the process is the evolution of heat.

The composition of hydrogen iodide can be determined by reaction with sodium amalgam as indicated for hydrogen chloride and hydrogen bromide. The vapour density is 63.94 ( $\text{H}_2 = 1$ ), corresponding with the formula HI.

### Iodides

Hydriodic acid resembles hydrobromic and hydrochloric acids, and forms salts—iodides. The iodides likewise resemble the chlorides and bromides, and they all can be prepared by similar processes. It is, however, worth noting that many of the so-called insoluble iodides precipitated by adding a solution of potassium iodide to a solution of

a metallic salt are soluble in an excess of a solution of potassium iodide. Most metallic iodides when heated in air furnish the metal or a metallic oxide and liberate free iodine. The iodides are usually less volatile than the corresponding chlorides and bromides. Many iodides have characteristic colours.

### Detection and Determination

Hydriodic acid and iodides are detected by the formation of a pale yellow curdy precipitate with silver nitrate, insoluble in dilute nitric acid and in ammonia. They also give free iodine when warmed with concentrated sulphuric acid, the element being recognized by its violet vapour. Iodides may be determined gravimetrically by precipitation as silver iodide, which is weighed as such. Volumetrically, the iodine liberated by means of a suitable oxidizing agent (cf. page 567) is titrated with a standard solution of sodium thiosulphate.

### § 25 Oxides of Iodine

Three oxides of iodine have been described:

Iodine Dioxide,  $\text{IO}_2$  or  $\text{I}_2\text{O}_4$ ,  
 $\text{I}_4\text{O}_9$ ,  
 Iodine Pentoxide,  $\text{I}_2\text{O}_5$ ,

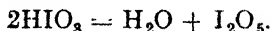
of which the last-named is the only important one. Also a number of other oxidized compounds of iodine have been reported which are probably mixtures.

**Iodine dioxide**,  $\text{IO}_2$  or  $\text{I}_2\text{O}_4$ , is said to be formed as a lemon-yellow powder by the action of cold nitric acid on iodine; also by the action of hot concentrated sulphuric acid on iodic acid. It readily decomposes into iodine and iodine pentoxide on warming.

$\text{I}_4\text{O}_9$  is said to result from the action of ozone on dry iodine.

### Iodine Pentoxide, $\text{I}_2\text{O}_5$

When iodic acid is heated to about  $170^\circ$  it decomposes with loss of water forming iodine pentoxide:



It is a white, crystalline solid which dissolves in water, re-forming iodic acid. It is more stable than any of the oxides of chlorine or bromine, although it decomposes into its elements above  $200^\circ$ .

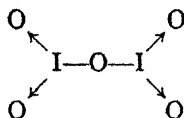
It is a powerful oxidizing agent and has the valuable property of being able to oxidize carbon monoxide to carbon dioxide, particularly in the complete absence of water



This reaction is applied to the detection and determination of carbon monoxide in small quantities when mixed with other gases. A reagent

for this purpose, known as "hoolmanite," is made from a mixture of iodine pentoxide, fuming sulphuric acid and powdered pumice.

The structure of this oxide is probably



### § 26 Oxyacids of Iodine

Three oxyacids of iodine are known in the form of their salts, viz.:

Hypoiodous Acid, HOI,

Iodic Acid,  $\text{HIO}_3$ ,

Periodic Acid,  $\text{HIO}_4$ ,

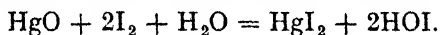
but periodic acid itself has probably not been isolated. In addition, many salts are known having complicated formulae derived from periodic acid (see below).

#### Hypoiodous Acid, HOI. Hypoiodites

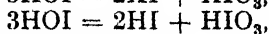
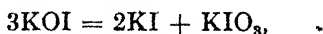
Iodine will dissolve in cold aqueous alkaline solutions, forming a liquid which has bleaching properties and is believed to contain hypoiodites in solution:



A dilute solution of the corresponding acid can be made by shaking mercuric oxide with a cold aqueous solution of iodine:



These solutions are very unstable and decompose on standing, forming first iodide and iodate, which (in the case of the free acids) react together with deposition of free iodine:



#### Iodic Acid, $\text{HIO}_3$ . Iodates

**Potassium iodate**,  $\text{KIO}_3$ , can be made by the direct action of potassium chlorate on iodine in presence of a little nitric acid, as represented by the equation:



This reaction is sometimes considered to be a direct replacement of chlorine, but it is more probably one of oxidation of iodine by the chlorate. This is a convenient method for the preparation of potassium iodate.

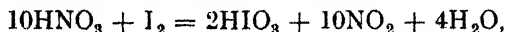
**Barium Iodate,  $\text{Ba}(\text{IO}_3)_2$** 

This salt can be prepared by dissolving iodine in an aqueous solution of barium hydroxide, or by the addition of barium chlorate to an aqueous solution of potassium iodate. White granular barium iodate is precipitated.

**The Preparation of Iodic Acid,  $\text{HIO}_3$** 

Iodic acid can be made by the processes described for bromic acid (page 563), of course substituting iodine for bromine, for instance, by the action of dilute sulphuric acid on barium iodate; or by the action of chlorine on water containing iodine in suspension; or by the action of an aqueous solution of chloric acid on iodine. Iodic acid, however, is usually made by the direct oxidation of iodine with nitric acid.

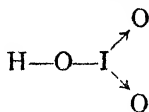
The reaction is represented by the equation:



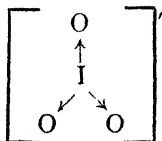
but it is no doubt much more complex.

The powdered iodine is added in small quantities at a time to concentrated colourless nitric acid; a current of air or carbon dioxide being passed through the apparatus to remove oxides of nitrogen as fast as they are formed. After the iodine has all dissolved and its colour has disappeared, the mixture is allowed to cool and the iodic acid, which separates, is filtered off on an asbestos filter. It is re-crystallized from dilute nitric acid.

The structure of this acid is represented as



giving rise thus to the ion



which is probably pyramidal in shape.

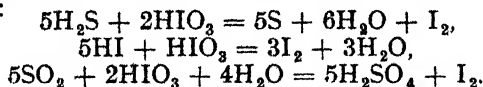
**Properties**

Iodic acid is a white crystalline solid, readily soluble in water. The aqueous solution first reddens blue litmus and then bleaches the colour. It does not give a blue colour with starch. It forms salts, the **iodates** which resemble the chlorates and bromates in many ways, but are less easily decomposed by heat. A series of *acid iodates* is known, for example,  $\text{KH}(\text{IO}_3)_2$ ;  $\text{KH}_2(\text{IO}_3)_3$ .

These are known only in the solid state; they are probably addition

compounds of iodic acid with the normal iodate resulting from the formation of hydrogen bonds (page 320).

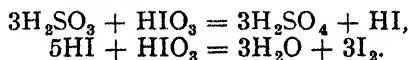
On heating, iodic acid passes into iodine pentoxide (see above). It is a strong oxidizing agent. It reacts, for example, with hydrogen sulphide, with hydriodic acid and with sulphur dioxide as indicated in the equations:



This latter reaction is used as a test for iodates. The solution is first acidified with hydrochloric acid to liberate the iodic acid, and then mixed with starch paste. Sulphurous acid, or an alkaline sulphite, is then added drop by drop. The liberated iodine forms "blue starch iodide," the characteristic reaction of iodine.

The reaction between sulphurous acid and an iodate is very interesting because the iodine does not appear immediately the substances are mixed; there is a well-defined period of time—period of induction—between the moment the reacting substances are mixed, and the moment iodine makes its appearance. The duration of the interval is dependent upon the concentrations of the solutions.

It is supposed that the first action is due to the reduction of the iodic acid to hydriodic acid; and when all the sulphurous acid has been oxidized this reaction is followed by the oxidation of the hydriodic acid by the excess of iodic acid:



(These two equations combined lead to the one quoted previously.)

The first reaction—oxidation of sulphurous acid—must be nearly completed before the second one can start, because, as indicated above, the iodine with sulphurous acid re-forms hydriodic acid. Since the maximum amounts of iodic and sulphurous acids are present at the start, the first-named reaction must be fastest at the beginning and afterwards gradually slow down. Again, since the velocity of a reaction is proportional to the concentration of the reacting substances present in the system, the second reaction will be the slowest at the start, and gradually become faster. The speed of formation of the iodine is therefore the resultant velocity of two consecutive reactions; and the belated appearance of the iodine—the period of induction—corresponds with the time required for the first reaction to make enough hydriodic acid to enable the second reaction to make sufficient iodine to colour the starch.

#### Periodic Acid, $\text{HIO}_4$ . Periodates

It is not certain if normal periodic acid— $\text{HIO}_4$ —has been made, but a large number of related salts, classed as periodates, is known. These are somewhat complicated in composition and are best understood as being salts of acids derived from the hypothetical iodine heptoxide— $\text{I}_2\text{O}_7$ —by addition of water step by step.

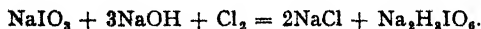
### Nomenclature of the Periodic Acids and the Periodates

When one anhydride forms a series of acids by union with different amounts of water, the acid containing most water is called the **ortho-acid**—from the Greek *ὀρθός* (*orthos*), regular; the other acids have prefixes, making **para-acid**—from the Greek *παρά* (*para*), beside; **meso-acid**—from the Greek *μέσος* (*mesos*), middle, intermediate; and **meta-acid**—from the Greek *μετά* (*meta*), beyond, less than the highest. Thus ortho-periodic acid would be  $\text{I}(\text{OH})_7$ , or  $\text{H}_7\text{IO}_7$ ; it is, however, not known. The only important periodic acid is **para-periodic acid**,  $\text{H}_5\text{IO}_6$  (corresponding to  $\text{I}_2\text{O}_7 + 5\text{H}_2\text{O}$ ). **Meta-period acid**,  $\text{HIO}_4$ , is also known and corresponds to  $\text{I}_2\text{O}_7 + \text{H}_2\text{O}$ . The **di-acids** are formed by loss of one molecule of water from two molecules of acid.

Thus, para-periodic acid on heating can be made to give **di-meso-periodic acid**,  $\text{H}_4\text{I}_2\text{O}_9$ , corresponding to the removal of one molecule of water from two molecules of meso-periodic acid,  $\text{H}_5\text{IO}_6$  (from  $\text{I}_2\text{O}_7 + 3\text{H}_2\text{O}$ ).

Periodates are known derived from meta-periodic acid, para-periodic acid, meso-periodic acid and from some poly-acids such as  $\text{H}_4\text{I}_2\text{O}_9$  and  $\text{H}_5\text{I}_2\text{O}_{11}$ .

**Di-sodium para-periodate**,  $\text{Na}_2\text{H}_5\text{IO}_6$ , can be prepared as a sparingly soluble salt by passing chlorine into an aqueous solution of sodium iodate and sodium hydroxide:

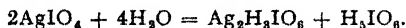


When this salt is dissolved in nitric acid and silver nitrate is added to the solution, crystals of **silver meta-periodate**,  $\text{AgIO}_4$ , separate when the solution is concentrated by evaporation.

### Para-periodic Acid

When silver meta-periodate is boiled with water, an insoluble salt, **secondary silver para-periodate**, is formed along with para-periodic acid,  $\text{H}_5\text{IO}_6$ .

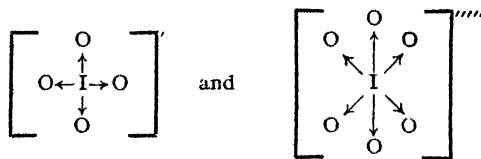
Thus



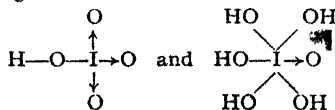
When the clear solution is concentrated, deliquescent crystals of the para-periodic acid are obtained. Para-periodic acid is also formed by the electrolytic oxidation of iodic acid with a lead dioxide anode (Hickling and Richards, 1940). This acid melts at  $133^\circ$ , and decomposes into iodine pentoxide, water, and oxygen at  $150^\circ$ . The water cannot be expelled by heat because oxygen is evolved along with the water. Periodic acid and neutral alkali periodates are reduced to iodates by hydrogen peroxide. Para-periodic acid is a more powerful oxidizing agent than iodic acid and is finding increasing use as a reagent in organic chemistry.

A small quantity of potassium periodate is said to occur in native Chile salt-petre, along with some sodium iodate.

The meta-periodate ion has been shown to be tetrahedral and the para-periodate ion octahedral. The electronic structure of these ions is believed to be



respectively corresponding to



for the acids.

The  $\text{IO}_4^-$  ion is tetrahedral; the  $\text{IO}_6^{3-}$  ion is octahedral.

### § 27 Interhalogen Compounds

The halogens form a considerable number of compounds among themselves, some of which are described below. These are known as Interhalogen Compounds.

**Chlorine monofluoride**— $\text{ClF}$ —is a colourless gas, obtained by the action of chlorine on hydrogen fluoride at the temperature of liquid air. It is very reactive, acting on some metals more vigorously than fluorine. It is also formed by the action of chlorine on fluorine at  $280^\circ$ ; when excess of fluorine is used in this experiment **chlorine trifluoride**— $\text{ClF}_3$ —results as a colourless gas of b.p.  $12^\circ$ . It is almost as reactive as free fluorine and as it can be stored as a liquid in steel cylinders it is coming into use in place of fluorine for the production of other fluorine compounds.

**Bromine trifluoride**— $\text{BrF}_3$ —is a colourless liquid, formed by the action of fluorine on bromine or hydrogen bromide; **bromine pentafluoride**— $\text{BrF}_5$ —is obtained similarly with excess of fluorine. It is a colourless solid.

**Bromine monofluoride**— $\text{BrF}$ —formed from the trifluoride and bromine as an unstable red-brown liquid has also been reported.

**Bromine chloride**— $\text{BrCl}$ —is said to be present in a mixture of chlorine and bromine vapour, and a solid hydrate,  $\text{BrCl} \cdot 4\text{H}_2\text{O}$ , has been described as crystallizing out when chlorine is passed into bromine covered with water.

**Iodine pentafluoride**— $\text{IF}_5$ —results from the direct combination of iodine and fluorine, or by the action of fluorine on iodine pentoxide. It is a colourless solid which combines with potassium fluoride giving the salt  $\text{KIF}_6$  and which, when heated to  $300^\circ$  with more fluorine, forms a gas—**iodine heptafluoride**— $\text{IF}_7$ .

**Iodine monochloride**— $\text{ICl}$ —is a liquid, on casual inspection, indistinguishable from bromine, formed by passing chlorine over iodine. **Iodine trichloride**— $\text{ICl}_3$ —is obtained as a yellow solid, by the action of excess of chlorine on iodine. This substance is soluble in concentrated hydrochloric acid and the solution forms, with bases, salts known as **tetrachloroiodides**, e.g., **ammonium tetrachloroiodide** (page 442). **Iodine monobromide**— $\text{IBr}$ —is formed by direct combination of the elements and is a crystalline solid, closely resembling iodine in appearance.

### § 28 Salts of Iodine

Since iodine is the heaviest member of the Halogen Group of elements (apart from astatine, *vide sub.*) it might be expected to show indications of the beginning of metallic properties; it being a general phenomenon that metallic character is more developed in the heavier than in the lighter elements of a group (cf. Chapter 9).

This is found to be the case here since iodine forms a number of compounds of a salt-like nature, in which the iodine is the electropositive part of the molecule. Among these might be included the chlorides of iodine mentioned in the preceding section. The following compounds have also been reported, viz.:

Iodine phosphate,  $\text{IPO}_4$ ,  
Iodine acetate,  $\text{I}(\text{C}_2\text{H}_3\text{O}_2)_3$ ,  
Iodine nitrate,  $\text{I}(\text{NO}_3)_3$ ,  
Iodine perchlorate,  $\text{I}(\text{ClO}_4)_3$ ,  
Iodyl sulphate  $(\text{IO})_2\text{SO}_4$

### § 29 Astatine. Atomic Number 85

When Mendeléeff first put forward the Periodic Table in 1869 (page 129) he left gaps corresponding, as he believed (rightly as we now know), to then undiscovered elements. One of these gaps occurred below iodine and was called *eka-iodine*. In terms of modern theory this is an element of atomic number 85 and it was searched for in residues from

the production of iodine and in similar places since it was believed that it would occur in association with iodine. Present-day theories of the nucleus, however, suggest that eka-iodine must be radioactive; if such a radioactive element has a short half-life it will not be found naturally unless it occurs as one of a radioactive series. In 1940, this element, to which the name **astatine** has been given, was obtained by Segré by the bombardment of bismuth with  $\alpha$ -particles. Since that time it has been detected among the disintegration products of the natural radioactive series. The isotope obtained by bombardment of bismuth is  $^{211}_{85}\text{At}$  and it has a half-life period of 7.5 hours. Its chemical properties have been investigated by Segré *et al.* (1949). So far as it has been possible to determine (the maximum concentration of the element available for investigation was of the order of  $10^{-8}$  molar) its properties seem to be those of a halogen occupying the position it does (At. No. 85) in the Periodic Table.

### § 30 The Halogen Family of Elements

The halogens (fluorine, chlorine, bromine and iodine) constitute the B sub-group of Group VII of the Periodic System (page 125). The corresponding A sub-group comprises the elements manganese, masurium and rhenium, and the relationship of these to each other, and to the halogens, will be discussed in Chapter 37.

Astatine has been obtained only in such minute quantity that insufficient is known of its chemistry at present to make it possible to include it in the discussion in this section.

The halogens themselves form a remarkable family of elements.

The gradation in characters which the halogens show with increasing atomic weights from fluorine to iodine yields an almost perfect family series. The family relationship of the halogens is illustrated by:

(1) The *similarity* in the chemical and physical properties of the elements and their corresponding compounds is such that the properties of any one member of the family can be said to summarize or typify the properties of the other members of the series.

TABLE XXXIV.—SOME PROPERTIES OF THE HALOGENS

Property	Fluorine	Chlorine	Bromine	Iodine
Atomic weight . . .	19	35.457	79.916	126.91
State of aggregation	Gas	Gas	Liquid	Solid
Melting point . . .	-223°	-101°	-7.3°	+113°
Boiling point . . .	-187.9°	-34.1°	58.8°	184.35°
Specific gravity . . .	1.08 (liq.)	1.55 (liq.)	3.19 (liq.)	4.93 (sol.)
Atomic volume* . . .	16.7	22.9	25.1	25.7
Colour of gas . . .	Pale yellow	Greenish yellow	Brownish red	Violet
Solubility (100 grams water at 20°) dissolves grams .	Decomposes water	1.46	4.15	0.0162

\* Atomic volume is the atomic weight divided by the specific gravity.



(2) The *gradual transition* of chemical and physical properties is such that if the elements be arranged in order: F, Cl, Br, I, the variation in any particular property in passing from fluorine to iodine nearly always proceeds in the same order, and that is the order of their atomic weights.

The relationship in the physical and chemical properties of the halogens is indicated in Table XXXIV.

All the halogens form compounds with hydrogen, and the readiness with which union occurs decreases as the atomic weight increases. The properties of the halogen acids and their salts show as striking a relationship as the elements themselves, and are shown in Table XXXV.

TABLE XXXV.—THE PROPERTIES OF THE HALOID ACIDS

Property	Hydrogen fluoride	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide
Molecular weight . . .	20	36.46	80.93	127.92
Boiling point . . .	19.4	-83.7°	-67°	-35.4°
Melting point . . .	-92.3°	-112°	-88.5°	-50.8°
Solubility in water . . .	35.3%	42%	49%	57%
Specific gravity saturated aq. sol at 20° . . .	1.15	1.19	1.49	1.70
Boiling point aq sol . . .	120° (36%)	110° (20%)	126° (47%)	127° (57)%
Dissociates at . . .	—	1500°	800°	180°
Heat of formation (Cals) . . .	+ 38.5 gas	+ 22.0 gas	+ 8.4 gas	- 6.4 gas
Heat of formation of K salt (Cals) . . .	110.6	105.7	95.3	80.1
Heat of neutralization NaOH . . .	16.3 cals	13.9 cals	13.84 Cals	13.78 Cals
Potassium salt melts . . .	885°	776°	730°	723°
Calcium salt melts . . .	1360°	772°	760°	575°
Solubility Ag salt (20°) per 100 gm. water . . .	172	0.00154	0.000084	0.000028
Solubility Ca salt per 100 ml solution . . .	0.0016	42.7	58.8	67.6

Taking almost any property and comparing its magnitude in passing from fluorine to iodine, or from fluorides to iodides, a similar gradual transition will be observed.

The boiling point of the acid and the composition of the mixture of hydrofluoric acid and water of constant boiling point are, however, exceptional. Hydrogen fluoride appears to be associated below 88°. Again, while the affinity of the halogens for hydrogen decreases with increasing atomic weight, the reverse tendency occurs with oxygen and the relationship is not so clearly defined. Thus, although fluorine forms two oxides—F<sub>2</sub>O and FO—numerous compounds of oxygen with chlorine have been obtained; and, judging by the known compounds with oxygen, the affinity of bromine for oxygen appears to be less, not greater, than is the case with chlorine. Chlorine, bromine, and iodine unite with one another forming an unstable series of compounds

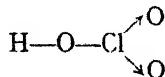
analogous, in some ways, with hypochlorites and chlorates, but the bromine analogue of perchlorates has not been prepared.

It is found when elements are compared that frequently the first element in any group (i.e., the element in the first short period) exhibits properties which cause it to resemble fairly closely an element in a neighbouring group, and make it, to some extent, separate from the rest of the members of its own group. Some of the properties of fluorine mentioned above illustrate this; for example, the weakness and association of the hydracid and also the solubility of the silver and calcium salts.

In many respects fluorine shows considerable resemblance to oxygen. Thus, the heats of formation of many fluorides are nearer to those of the corresponding oxides than of the chlorides; while the fluorides and oxides resemble each other in solubility, volatility and fusibility more closely, as a rule, than the fluorides and chlorides do. These statements are well illustrated by a comparison of hydrogen fluoride and water. Thus the equivalent heat of formation of water (34.2 Cals.) is closer to that of hydrogen fluoride than to that of any other halogen hydracid; the boiling point of hydrogen fluoride is nearest to that of water and its range of fluidity most nearly similar. Like water too it is, by comparison with the other hydrogen compounds, a weak acid.

Another point of similarity between fluorine and oxygen is the fact that the fluorides and oxides of the elements are usually compounds in which the element exhibits a higher stable valency than in the chlorides. Thus, for example,  $\text{SO}_3$  and  $\text{SF}_6$  are stable compounds at ordinary temperatures, whereas  $\text{SCl}_6$  cannot exist at ordinary temperatures, and a number of other similar cases could be cited. Again, fluorine will combine directly with carbon (as does oxygen) while the remaining halogens are without effect on it.

The observed behaviour of the halogens is well supported by the electronic structure now assigned to these elements in which the outermost, or valency, group of electrons contains seven electrons; only one fewer than in the next Inert Gas. They are, therefore, all strongly electronegative because they readily acquire an additional electron, thus acquiring the structure of an Inert Gas. This accounts for the vigorous formation of monovalent anions; also for monocovalent molecules such as  $\text{Cl}_2$  and  $\text{HCl}$ . The formation of compounds of the halogens of higher covalency than one involves the use of unshared electron pairs of the halogen atom acting as donors; for example in the chlorates:



Compounds such as iodine pentafluoride or iodine heptafluoride involve the expansion of the valency group beyond eight.

Fluorine is the most powerfully electronegative element known, the remaining halogens following next in order. This fact is accounted for

by the small size of the fluorine atom. The formation of the fluorine ion, for example, depends upon the attraction of the positive fluorine nucleus on an electron of another atom so that it becomes transferred and attached to the fluorine atom, thus forming a stable octet. The smaller the halogen atom concerned the nearer will its nucleus be to this electron and the greater, therefore, its pull. It is true that with halogen atoms of larger atomic number the charge on its nucleus is correspondingly greater, but so is the screening cloud of electrons as well as the diameter of the halogen atom.

## CHAPTER 26

# THE ATMOSPHERE

### INCLUDING THE INERT GASES

I conceive the confused mass of vapour, air, and exhalations which we call the atmosphere, to be nothing else but the particles of all sorts of bodies of which the earth consists, separated from one another and kept at a distance by repulsive forces.—ISAAC NEWTON (1717).

#### § 1 General

FROM very early times the air was regarded as an element, though it is open to question whether the conception of an element was then the same as ours in the chemical sense (cf. page 5). The presence of water vapour was also recognized very early, but it was not thought of as an essential part of the atmosphere.

Mayow (1674) was probably the first to produce reliable evidence for the composite nature of the atmosphere. He showed that a mouse confined in a bell-jar over water causes a diminution in the volume of the air, and also that the same result occurs when combustible substances are burned under similar conditions. He also showed that the residue of gas after these experiments is unfit both for breathing and for combustion. The presence of carbon dioxide in the air was established by Black in 1755, who called it *fixed air*.

The real nature of the atmosphere remained obscure until the time of Lavoisier, chiefly owing to the then prevailing phlogiston theory (see Chapter 1, page 9). According to this theory, combustion was attended by the escape of phlogiston, a calx remaining. The original substance could often be regenerated by heating these calces with a substance rich in phlogiston (e.g., copper calx and carbon give the metal again). That the air played some part in this process was indicated by experiments such as those of Mayow, but this was explained by assuming that something had to be present to take up the escaping phlogiston, and that air which would no longer support combustion was "saturated with phlogiston."

As was pointed out in Chapter 1, this theory, although erroneous, played an important part in the development of chemistry, but naturally, so long as it held the field, the elemental nature of the air was not seriously questioned.

The true nature of air and the correct theory of combustion were not understood until the work of Lavoisier directed attention to the increase in weight of substances after burning, and led to a correct interpretation of Priestley's discovery of oxygen.

## § 2 Lavoisier's Experiments on the Composition of Air

Antoine Laurent Lavoisier (1774) extended experiments which had been described by Rey in 1630 with more decisive results. Lavoisier heated tin along with air in a *closed* vessel. The vessel containing the air and tin did not increase in weight, although part of the air was absorbed. When the flask was opened, air rushed in, and the increase in the weight of the vessel was found to be equal to the increase in weight which the tin alone had suffered. Hence, Lavoisier concluded with Rey that the increase in the weight of the tin was due solely to an absorption of the air in which the calcination had occurred. There was not sufficient air in the flask to "saturate" all the tin, and yet some air always remained as a residue. Hence, Lavoisier concluded further that **only part of the air can combine with the metal during the calcination**; he also found that *the increase in the weight of the tin during calcination is equal to the decrease in the weight of the air*. Hence, it seems as if air contains at least two constituents, only one of which is absorbed by the heated metal.

Lavoisier continued this important work with mercury instead of tin. The mercury was confined in a retort with an S-shaped neck which dipped under a bell-jar in a trough of mercury, as illustrated in Fig. 26.1. The air in the retort was in communication with the air in the bell-jar. The level of the mercury in the bell-jar was adjusted at a convenient level, and its position "very carefully marked with a strip of gummed paper." By means of a charcoal furnace, the mercury in the retort was heated—not quite to its boiling point. Lavoisier said: "Nothing of note occurred during the first day. The second day I saw little red particles\* swimming over the surface of the mercury, and these increased in number and volume during four or five days; they then stopped increasing and remained in the same condition. At the expiration of twelve days, seeing that the calcination of the mercury made no further progress, I put the fire out." After making allowance for variations of temperature and pressure, Lavoisier noticed that the volume of air in contact with the mercury was about 50 cubic "inches," and after the experiment, between 42 and 43 cubic "inches." About one-sixth of the volume of air in the apparatus was absorbed by the mercury.†

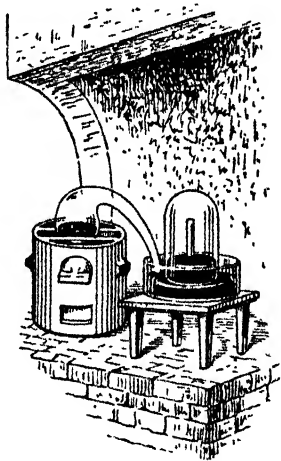


FIG. 26.1  
Lavoisier's Experiment on  
the Composition of Air

\* The calx or oxide of mercury is red. It is now called "red oxide of mercury" or "mercuric oxide."

† More recent experiments show that one-fifth is nearer the mark.

The air which remained in the retort was not absorbed by the hot mercury; it extinguished the flame of a burning candle immersed in the gas; and a mouse was quickly suffocated when placed in the gas. Hence, Lavoisier called the gas *azote*, "from the  $\alpha$  privative of the Greeks, and  $\xi\omega\eta$ , life." In France the gas is still "*azote*," though in Britain it is called "nitrogen," and in Germany "*Stickstoff*," that is, "suffocating stuff."

About this time, Lavoisier heard of Priestley's discovery of oxygen (which Priestley called *dephlogisticated air*) and at once perceived its significance in the light of his own experiments.

He collected the red powder formed by heating mercury in the retort, Fig. 26.1, and by reheating it in a suitable retort, Lavoisier obtained between seven and eight cubic "inches" of a gas which had obviously been previously removed from the air by the hot mercury. When a burning candle was immersed in the gas, the candle burnt with "blinding brilliancy," as Lavoisier expressed it; a smouldering splinter of wood burst into flame when plunged in the gas; and the gas did not suffocate a mouse like *azote*. Lavoisier first called this gas *vital air*, and afterwards *oxygen*. The latter term is its present-day designation. In this manner, Lavoisier proved that **atmospheric air is made up of two gases—oxygen and nitrogen—of different and even opposite natures; the oxygen alone combines with the metal during calcination.**

Assuming that this interpretation of the experiments is correct, Lavoisier inferred that by mixing *azote* and oxygen in the right proportions, it ought to be possible to reproduce atmospheric air. This Lavoisier did, and the mixture was found to behave with respect to "combustion, respiration, and the calcination of metals similarly in every respect to atmospheric air."

In addition to these constituents and the carbon dioxide recognized by Black, in 1777, Carl Wilhelm Scheele inferred that air also contains a little ammonia, because a bottle of hydrochloric acid, when exposed to the air, becomes covered with a deposit of sal-ammoniac (ammonium chloride).

The main constituents of the atmosphere were thus recognized to be oxygen, nitrogen, carbon dioxide and water vapour, with possible traces of ammonia. In addition to these, it is now known that all manner of other substances occur in traces, e.g., hydrogen, hydrocarbons, hydrogen peroxide, carbon dioxide, sulphur compounds, organic matter, suspended solids, chlorides, ozone, water vapour, argon, helium, krypton, neon, xenon. The five gases last named are sometimes called the "noble gases" or the "inert gases" of the atmosphere, and are discussed below (page 588). **Dust** is also common in air. The Report of an Advisory Committee on Atmospheric Pollution (1925) states that the smallest number of particles counted (on a very clear day) in the outside air in London was 300 per c.c., while the largest number (on a foggy day) was 60,000. By comparison the smallest and

largest counts at Athens were 40 and 4,300. Napier Shaw (1925) gives the normal amount of solid matter in the atmosphere of London as varying between 0.1 milligram and 1 milligram per cubic metre. Counts made in Oxford during the past few years have yielded the figures 0.03 mgm. to 0.8 mgm. per cubic metre. Over the Pacific Ocean from 280 to 2200 per c.c. have been counted. **Micro-organisms** of various kinds abound in the lower strata of the atmosphere. These cause putrefaction, fermentation, and pathological phenomena. When filtered through asbestos or cotton-wool, air is freed from dust particles, and when a beam of light is passed through dust-free air, it will no longer reveal a multitude of motes constantly in motion. The space is optically empty.

### § 3 The Constituents of the Atmosphere

#### Oxygen and Nitrogen

Some of the early workers believed that the proportion of oxygen and nitrogen in air varied with respect to time and place, as well as the state of the weather; but the analyses of Cavendish, Macarty, Sir H. Davy, and C. L. Berthollet rendered it highly probable that only a minute difference is to be found in the proportions of these two elements with air collected in different localities, and this is confirmed by analyses conducted more rigorously with all the refinements known to chemists.

The following analyses are quoted to illustrate the percentage amount of oxygen in air (by volume).

Locality	Mean	Number of analyses	Analyst
Scotch Hills .	20.97	34	R. A. Smith
Paris . . .	20.96	100	V. Regnault
Dresden . .	20.93	46	W. Hempel
Cleveland, Ohio	20.93	45	E. W. Morley
Boston (Mass.)	20.952	212	F. G. Benedict
Ocean air . .	20.946	36	"
Pike's Peak .	20.945	5	"

Hence, after making due allowance for differences in the methods of analysis by different men, it is clear that **the relative proportions of nitrogen and oxygen in the air collected near sea-level are almost, but not quite, constant.**

#### Carbon Dioxide

Similar remarks apply to the amount of carbon dioxide. This is rather higher in towns than in the open country; but diffusion of air by winds, etc., prevents an excessive accumulation in any part—excluding, of course, badly ventilated rooms. Thus a very careful

estimate by Krogh (1917) gives 0.03 per cent  $\pm$  0.0025 as the average value. Haldane (1936) found variations in the amount present in country air from 0.021 per cent to 0.044 per cent, while the mean of 152 observations near Perth gave the value 0.0324 per cent. Callendar (1940) has shown that the proportion of carbon dioxide in the atmosphere has increased by about 30 parts per million during the last fifty years; this is said to be equal to the amount produced by the combustion of fuels during the same period. The air over the Antarctic ocean contains about 2.56 parts of carbon dioxide per 10,000 parts of air (Muntz and Aulien (1886)). This is rather less than has been noted elsewhere. The other constituents—excluding moisture—are usually regarded as impurities. The constituents of normal or average air occur in the following proportions (Carpenter *et al.*, 1937):

TABLE XXXVI.—AVERAGE COMPOSITION OF ATMOSPHERIC AIR

Per cent of	By weight	By volume
Nitrogen . . . . .	75.517	78.095
Oxygen . . . . .	23.140	20.939
Inert gases . . . . .	1.284	0.933
Carbon dioxide . . . . .	0.047	0.031

### Ozone, Hydrogen Peroxide, and Nitrogen Oxides

It is now believed that most of the ozone in the atmosphere is generated in the stratosphere (about 30 miles up) by the action of short-wave radiation from the sun. Hydrogen peroxide is probably formed by electrical discharges in the atmosphere; the same remark applies to the oxides of nitrogen. Free nitric acid has been reported in the atmosphere of tropical regions, but generally, the nitric acid is combined with ammonia. There is no doubt that much combined nitrogen in the form of ammonium compounds and nitric acid is returned to the ground by the rain, but the estimates of the amounts vary widely both with the locality and with the observer. Thus, N. H. J. Miller (1905) gives figures varying from 2.71 lb. of ammonia per acre per annum at Rothamsted to 14.03 lb. per acre per annum in Venezuela; the corresponding amounts for nitric acid being 1.13 lb. at Rothamsted and 5.2 lb. in Venezuela. Similarly variable figures have been given by Drover (1956) and others.

### Ammonia

The ammonia in the atmosphere is largely a product of organic decomposition, and it is returned to the earth by rain in the form of ammonium nitrate, and sometimes as ammonium sulphate or chloride.

### Hydrogen and Hydrocarbons

A. Gautier (1901) found that the air of Paris contains per 100 litres: 19.4 c.c. of free hydrogen, 12.1 c.c. of methane, 1.7 c.c. of benzene and



related hydrocarbons, and 0.2 c.c. carbon monoxide with other hydrocarbons. Gautier's estimate is probably rather high. H. Henriet (1904) found 2 to 6 grams of formaldehyde per 100 cubic metres of air. The presence of hydrocarbons explains the oleaginous character of the deposits which form on roofs, leaves of trees, etc., in towns.

### Sulphur Compounds

During two years of observations at Oxford recently the sulphur dioxide content of the air was found to vary from 0.4 parts per hundred million of air to 28.8 parts per hundred million. Another source quotes figures for Chicago of 6 to 27 parts per hundred million in a residential district and 40 to 50 parts per hundred million in a manufacturing area. Sulphur compounds are also present in small quantities as hydrogen sulphide and sulphuric acid in the air of towns. According to Mann (1955) 6.96 lb. of sulphur (in the form of sulphuric acid) per acre per annum is "poured" on the ground at Rothamsted. C. E. Miller (1955) quotes figures for various parts of the U.S.A. which vary from 4.2 to 27 lb. of sulphur per acre per annum.

### Chlorine Compounds

Rain near the sea brings a certain amount of chlorine derived from the sea-water. The proportion of salt in the air is greatest near the sea, and diminishes rapidly farther away from the coast. E. Kinch (1900) found, as an average of twenty-six years' observations at Cirencester, that 36.1 lb. of sodium chloride per acre were brought to the earth with the rain. The amount of "wind-borne" sea salt is greatest when the wind blows from the sea. Free hydrochloric acid derived from manufacturing operations is sometimes found in the air of towns.

### Moisture

The average amount of moisture, aqueous vapour, in air is rather less than 1 per cent by volume; it may reach 4 per cent in humid climes. The actual amount of aqueous vapour air can carry before it is saturated depends upon the temperature. The higher the temperature, the greater the amount of moisture air can carry.

## § 4 Is Air a Mixture or a Compound ?

It is not quite clear to what extent the compound nature of air was seriously believed in, but there seems no reason to doubt that for a period after Lavoisier the possibility was at least seriously considered. Consequently, it is of some importance to consider the arguments which are now held to demonstrate conclusively that air is a mixture.

These arguments may be summarized as follows:

- (i) Although the proportions of nitrogen and oxygen show remarkably

U\*

little variation, variations do in fact occur which lie outside the range of experimental error.

(ii) The characteristic properties of air are those which would be expected for a mixture, in the known proportions, of oxygen and nitrogen, being a mean between those of the constituents. In general, it is known that the physical properties of compounds bear little, if any, resemblance to those of their constituents.

(iii) No heat, no change in volume, or any other sign of chemical change is observed when air is made artificially by mixing oxygen and nitrogen together in the right proportions, and the mixture behaves like air.

(iv) The constituents of air can be separated by mechanical means: e.g., solution in water (page 191); by diffusion (page 34); by allowing liquid air to vaporize, when the nitrogen distils off before the oxygen (page 49); and J. Dewar has shown that when solidified air is exposed to a magnetic field the oxygen is sucked out of it towards the magnet's poles "so that solid air appears to be a magma of nitrogen and oxygen" separable by a magnet.

(v) The formula of air, if a compound, would be about  $N_{16}O_4$ , or possibly  $N_4O$ . In either case the vapour density of such a gas would be many times that found for air.

Not one of these five reasons is in itself conclusive, but all, taken together, form a long chain of circumstantial evidence which leads to the verdict: Air is a mechanical mixture of nitrogen, oxygen, etc.

### § 5 The Analysis of Air

The gravimetric analysis of air is effected by the method used for preparing nitrogen from the air (page 422). It was done in this way by J. B. A. Dumas and J. Boussingault (1841) in an apparatus similar in principle to that illustrated in Fig. 26.2 where a modern furnace is

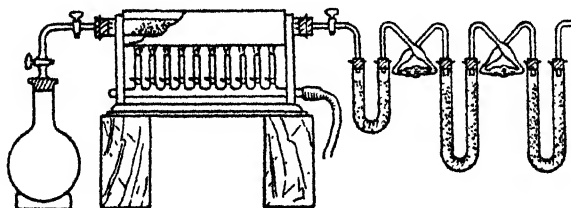


FIG. 26.2 —Diagram illustrating the Principle of Dumas and Boussingault's Method for the Gravimetric Analysis of Air

shown in place of the old charcoal furnace, and the number of drying tubes has been reduced. A large globe was evacuated, closed, and weighed in that condition. This globe was connected as indicated in Fig. 26.2, to a tube containing metallic copper also evacuated, closed,

and weighed. The copper tube was connected with a series of bulbs, and tubes containing concentrated sulphuric acid to remove moisture and ammonia from the air; and with potassium hydroxide to remove carbon dioxide—only a few of the tubes used by Dumas and Boussingault are shown in the diagram. There may be a witness tube to show that the air which passes into the hot tube is free from carbon dioxide and moisture. The tube containing the copper was heated red hot, and air allowed to enter slowly by gradually opening the stopcocks. The air on its way to the glass globe was deprived of all but the nitrogen (atmospheric). When the globe was full, the apparatus was cooled, and the globe weighed. The increase in weight gave the amount of nitrogen in the globe. The tube containing the copper, now partially oxidized, was also weighed. Its increase in weight represented the weight of oxygen which was associated, as air, with the nitrogen in the glass globe; the tube also contained some nitrogen. The tube was therefore exhausted and weighed again. The difference between the second and third weighings of the tube was taken to represent the nitrogen which must be added to the nitrogen in the globe.

As a mean of six determinations they obtained 23.005 grams of oxygen per 76.995 grams of nitrogen. The gravimetric process is very exact. The error need not exceed 0.00001th part of the whole; but the experiment requires special apparatus, and occupies much time. Volumetric processes are not so exact, but they occupy far less time.

### Volumetric Processes

Of volumetric processes, the most accurate is to explode a mixture of a measured volume of air and excess of hydrogen confined over mercury in a eudiometer. The hydrogen combines with the oxygen to form water, which condenses, so that one-third of the contraction which occurs is equal to the volume of oxygen present initially.

Another convenient method is by means of Hempel's apparatus (Fig. 26.3). This consists of a levelling tube *L* and a burette *E* connected by means of capillary tubing *D* to a Hempel pipette *ABC*. The pipette contains a solution of 10 grams of pyrogallic acid in 200 ml. of a solution made from 160 grams of potassium hydroxide and 130 ml. of water. Enough water is poured into the levelling tube to fill the burette and the connecting rubber tubing. The levelling tube is then raised, the three-way tap *T* being turned so as to put the burette in communication with the air, until the burette is full of water.

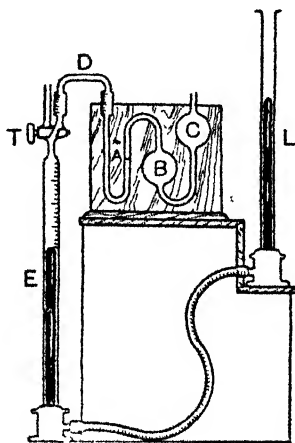


FIG. 26.3.—Hempel's Apparatus

A suitable volume of air is then drawn into the burette by lowering the levelling tube and the tap *T* is closed. The levels are adjusted and the volume of the air read off. The levelling tube is raised and the tap *T* is now turned carefully so as to put the burette and pipette into communication, thus driving the air over from the burette into the pipette until the water from the burette reaches about halfway up the right-hand portion of the capillary tube *A*. The tap *T* is then closed and the pipette gently rocked for five minutes. The tap is then turned again and the air brought back into the burette by lowering the levelling tube until the liquid from the pipette just fills the capillary tube *D* again. The tap is once more closed, the levels are adjusted and the volume of the air remaining is read. The process is repeated until no further change in volume occurs. The contraction in volume then represents the amount of oxygen present initially in the air.

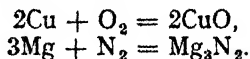
## § 6 The Inert Gases. History and Preparation

### History

In 1785 Cavendish subjected a sample of air to the action of electric sparks, and absorbed the oxides of nitrogen so formed in caustic alkali solution. When no more contraction would take place, he added more oxygen and continued the sparking. When, at length, even after the addition of yet more oxygen, no further contraction could be brought about, he removed the excess oxygen with liver of sulphur (potassium pentasulphide, page 643) and found that there remained a small bubble of gas which could not be absorbed by these processes. Cavendish concluded, as a result of these experiments, that "if there is any part of the phlogisticated air (= nitrogen) of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than  $\frac{1}{100}$ th part of the whole." This result obtained by Cavendish proved eventually to be remarkably accurate for the date at which it was obtained.

The importance of this observation was not realized for more than a hundred years until, in 1892, Lord Rayleigh, in the course of a series of very accurate determinations of the densities of some of the commoner gases, found that the density of nitrogen derived from the air by removal of oxygen, carbon dioxide, moisture, etc., was about 0.47 per cent greater than the density of nitrogen prepared from ammonia, etc. The difference is much larger than the experimental error involved in the determinations, and so some other cause was sought. Various suggestions were made, such as the presence of a heavy allotrope in atmospheric nitrogen (e.g.,  $N_3$ ) or of hydrogen in the chemical nitrogen; but these hypotheses were soon shown to be untenable and the cause of the discrepancy to be the presence of a hitherto unrecognized gas. This gas was isolated by Ramsay in 1894 by removing from air freed from carbon dioxide and water vapour, first, the oxygen by passing it

over heated copper, and then the nitrogen by passage over heated magnesium. Under these conditions:



The new gas, to which the name *argon* was given—from the Greek *ἀργός* (*argos*), inert or idle—was found to have a density of about 20 and to be chemically inert and apparently incapable of forming chemical compounds. Owing to its inertness, its atomic weight could not be found by chemical methods; but since the ratio of its specific heats (page 82) was found to be 1.67, it was concluded that it is monatomic and hence that its atomic weight is twice its density, i.e., 40 approximately.

These results encouraged Rayleigh and Ramsay to undertake further investigations, which soon led to the recognition of a whole family of Inert Gases, viz., helium, neon, argon, krypton and xenon, which were found to fit into the Periodic Table between the strongly electronegative halogens and the strongly electropositive alkali metals (see § 7 below).

The last member of this family is the radioactive gas, variously known as radon, thoron or actinon according as the isotope in question has resulted from the disintegration of radium, thorium X or actinium X. Radon was first recognized and investigated in 1902 by Rutherford and Soddy. With its discovery the family of Inert Gases became complete.

### Preparation

Helium is now extracted in quantity (see below) from natural gas and certain minerals; radon is obtained as a product of radioactive change; for the remaining members of the Inert Gas family the atmosphere is the only available source.

Two methods are available for this extraction, both of which were employed by Rayleigh and Ramsay during their investigations. These are:

- (i) the removal, by chemical means, of all other constituents;
- (ii) the fractionation of liquid air.

The **chemical method** of extraction by sparking derives, of course, from Cavendish and was much improved by Rayleigh and Ramsay, whose apparatus is shown diagrammatically in Fig. 26.4.

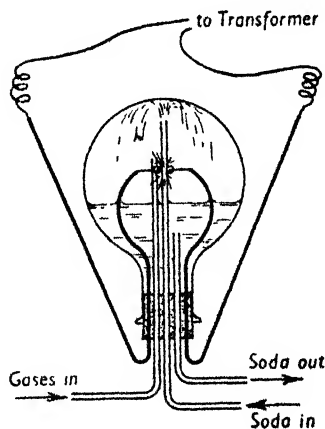
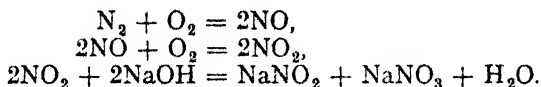


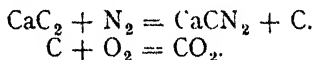
FIG. 26.4.—Rayleigh and Ramsay's Apparatus

It consists of a large flask of about 50 litres capacity, closed by a rubber stopper. It is furnished with two substantial platinum electrodes; with tubes for the circulation of strong caustic alkali solution, and with a tube for the admission of a mixture of air and oxygen, containing approximately 9 parts of air to 11 parts of oxygen. Cooling is effected by passing the alkali solution through a worm condenser. The alkali solution circulates in a closed system so that no argon is lost through solution in it. By this means, the nitrogen is removed from the air by combination with oxygen to form nitric oxide and nitrogen peroxide, as in the fixation of nitrogen by the arc process (page 444). The reactions which occur are indicated by the equations:



The argon (and other inert gases) accumulate in the flask. The complete separation of the higher members of the series from the argon is only effected by liquefaction and subsequent fractionation.

Ramsay also used hot magnesium for the removal of the nitrogen, but this reaction is very slow. A more efficient modification of this process is the use of calcium carbide, mixed with about 10 per cent of calcium chloride and heated to  $800^\circ$ . Both oxygen and nitrogen are absorbed according to the equations:



Industrially the inert gases are obtained **by the fractionation of liquid air**—a development of the method employed by Rayleigh and Ramsay in the later stages of their investigations. The boiling points of the various gases are, at 760 mm.:

Helium	.	.	.	- 268.9°
Neon	.	.	.	- 246.1°
Nitrogen	.	.	.	- 195.8°
Argon	.	.	.	- 185.9°
Oxygen	.	.	.	- 183°
Krypton	.	.	.	- 153.2°
Xenon	.	.	.	- 108.1°

from which it appears that the helium and neon have boiling points very considerably below that of nitrogen. In consequence, in the ordinary nitrogen separation process (page 49) these two gases escape liquefaction and there accumulates in the liquefying column, above the liquid, a mixture of nitrogen, neon and helium. This mixture is led through a spiral column situated in the stream of evaporating nitrogen, with the result that most of the nitrogen it contains is liquefied. The remaining nitrogen is removed by chemical means (e.g., with calcium carbide). The separation of the neon from the helium (the proportions are usually about 3 parts of neon to 1 part of helium) is then effected,

either by cooling in liquid hydrogen when the neon solidifies and the helium passes on, or by selective adsorption of the gases in charcoal at a low temperature. Commercial neon usually contains about 2 per cent of helium.

The boiling point of argon is very close to, and is not far above, that of nitrogen, hence its separation is difficult and is effected in a special type of column. Most of the argon is found in the liquid oxygen obtained in the air-liquefaction process. This mixture is run into the base of a fractionating column round a coil through which compressed air is being circulated. Partial evaporation occurs, the vapour being richer in argon than the liquid. This vapour travels up the column against a descending stream of liquid oxygen. Argon is thus removed from the descending liquid and oxygen from the ascending vapour. The same process is then continued in a second column; after which the last traces of oxygen (and nitrogen) are removed chemically.

## § 7 Helium, He

### Discovery and Preparation

In 1868, P. J. C. Janssen detected a prominent orange line in the spectrum of the sun's photosphere which did not correspond with the spectral line of any known element. Hence E. Frankland and J. N. Lockyer suggested the existence of a new element to which the name helium (from *ἥλιος*—*helios*—the sun) was given. The same line was later detected in the spectra of certain stars, and in 1882 Palmieri observed it in the spectrum of the gases flaming from Vesuvius.

In 1882 Hildebrand had reported the presence of a gas which he identified as nitrogen, occluded in certain minerals such as *cléveite* (a variety of pitchblende), *fergussonite*, *bröggerite*, *uraninite*, etc. After the discovery of argon it was suggested to Ramsay that he should examine this occluded nitrogen to see if it contained any argon. His examination showed that the gas contained no argon, nor did it consist of nitrogen but was, in fact, helium. A little later the presence of helium in the atmosphere was established; it has also been detected in the gaseous emanations from certain springs, and it occurs to the extent of almost 1 per cent in the natural gas of the U.S.A.

Helium is now an important article of commerce, particularly in the U.S.A., where it is extracted from natural gas and has been used for filling airships. Its extraction from certain minerals, in particular from monazite sand (which contains about 1 c.c. per gram of sand, page 805), is also assuming commercial importance. Its presence in these minerals is the result of radioactive changes taking place in certain constituents of the mineral. The helium is obtained from the natural gas by liquefaction and subsequent fractionation; it is removed from monazite sand by heating to 1000°.

### Properties

Helium is a colourless, tasteless and odourless gas, with a density of 2.001 ( $H_2 = 1$ ), so that, next to hydrogen, it is the lightest gas known. It can only be liquefied with the very greatest difficulty. Like hydrogen, it does not cool itself on expansion through a small jet at ordinary temperatures, and in fact must be cooled to  $-258^\circ$  before this process will work. It is, therefore, cooled first in boiling liquid hydrogen. It was first liquefied by Kamerlingh Onnes in 1907, and was solidified by Keesom in 1926. By the rapid evaporation of liquid helium, under reduced pressure, a temperature of only  $0.82^\circ$  above the absolute zero was reached.

In common with the other members of the Inert Gas family, helium is usually supposed to form no compounds, and hence its **Atomic Weight** has not been determined by chemical methods, although the existence of compounds with tungsten and mercury has been reported. Thus Boomer in 1925 claimed that electronic bombardment of helium in presence of tungsten leads to the formation of a compound,  $WH_2$ , and Manley in 1927 reported that when subjected to a glow discharge mercury in contact with helium forms  $HgHe$  or  $HgHe_2$ . The existence of these compounds has not been confirmed and is very doubtful.

The atomic weight of helium has been evaluated from the determination of the density and the ratio of the two specific heats of the gas. This latter ratio, as found from measurements of the velocity of sound in the gas, is 1.67, indicating that helium is monatomic, and hence has an atomic weight equal to twice its density compared with hydrogen. The value at present (1957) recommended by the International Committee is 4.003.

### Uses

Helium was used in the United States for filling airships for, although it is not so light as hydrogen, its lifting power is still 92 per cent of that of the latter gas, and it possesses the great advantage of non-inflammability. It also has the advantage over hydrogen of escaping less readily by diffusion through the material of the gas-bags. By reason of its very slight solubility in the blood it is being used as a diluent for oxygen in modern diving apparatus. The very considerable solubility of nitrogen in these circumstances causes the formation of bubbles in the blood when the pressure is released; a trouble known as caisson disease.

## § 8 Neon, Ne

### Discovery and Preparation

Neon was discovered in 1898 by Ramsay and Travers who suspected that a gap existed in the family of Inert Gases previously discovered. It was isolated by the liquefaction of 18 litres of crude argon and fractionation of the resulting liquid.



Neon is now manufactured from the atmosphere by liquefaction, as described above (page 590).

### Properties

Neon is a colourless, tasteless, odourless gas having a density of about 10.1 ( $H_2 = 1$ ). Hence its atomic weight (since it is found to be a monatomic gas) is 20.2 approximately. The value at present accepted by the International Committee is 20.183. It consists of a mixture of three isotopes of mass 20, 21 and 22 respectively, and was the first non-radioactive element for which unmistakable evidence of the existence of isotopes was obtained (cf. page 141).

### Uses

Neon is very extensively used in discharge tubes for advertising purposes, since, when subjected to a discharge at 1000 volts at a pressure of 2 mm., it emits a very bright and characteristic orange-red glow. A blue or green colour is similarly obtained by admixture of a little mercury vapour with neon. Argon and mercury vapour are similarly used for producing a blue or green colour, and the so-called ripple tubes contain a trace of an organic compound in addition to the Inert Gas or Gases.

## § 9 Argon, A

Argon is manufactured in considerable quantities from liquid air, as described previously.

It is colourless, tasteless and odourless; its density is 19.97 ( $H_2 = 1$ ); it is monatomic and its atomic weight is 39.944. Its atomic weight is thus higher than that of potassium, although it should be lower according to the relative positions of the two elements in the Periodic Table. This anomaly was for long unexplained, but is now known to be caused by the preponderance of the heaviest of the three isotopes of which argon is composed (page 144). Argon is appreciably soluble in water, more so than either oxygen or nitrogen. It is not known with certainty to form any compounds, although the existence of a hydrate  $A.5$  or  $6H_2O$  has been reported (Villard, de Forcrand, 1902) and Booth and Wilson (1935) obtained a freezing-point curve for mixtures of argon and boron trifluoride which was thought to indicate the existence of a series of compounds  $A.(BF_3)_x$  where  $x = 1, 2, 3, 6, 8$  or  $16$ . Recent work has shown that argon and boron trifluoride are not miscible and so has cast great doubt on the existence of these compounds.

Powell (1950) has described the production of substances to which he gave the name "clathrate compounds" by allowing quinol (hydroquinone) to crystallize slowly from water in presence of argon, krypton or xenon under pressure. The inert gas atoms are then found to be trapped in cages in the giant-molecule type of crystal and the products are completely stable in the solid state. X-ray investigations show that

in the clathrate "compound" containing argon the distance between the argon atoms is about the same as if the gas were confined at a pressure of about 70 atmospheres.

It is now believed that the hydrates of the Inert Gases, such as that of argon mentioned above, are also clathrate compounds like the hydrates of methane and ethylene.

### Uses

Argon is used to some extent, as mentioned above, in discharge tubes for illumination; but its principal use at present is in the manufacture of "gas-filled" lamps, in which it is very much more efficient than nitrogen, probably on account of its monatomicity.

### § 10 Krypton and Xenon, Kr and Xe

Krypton and Xenon were discovered by Ramsay and Travers in the final residues from the evaporation of liquid air. They are present only in very minute proportions in the atmosphere and so far have not found any practical applications. Their use in place of argon in electric lamps is said to increase still further the efficiency of the lamps and a projection lamp in which an arc is struck in an atmosphere of xenon has recently been marketed and for which an exceptionally high efficiency is claimed. The extraction of xenon in sufficient quantity involves the handling of enormous quantities of air. Hydrates of both elements have been reported.

The proportions of the Inert Gases present in the atmosphere are given in Table XXXVII.

TABLE XXXVII.—PROPORTIONS OF  
INERT GASES IN AIR

Gas	Number of volumes of air containing 1 volume
Helium	190,000
Neon	55,000
Argon	107
Krypton	1,000,000
Xenon	12,500,000

Very accurate determinations of the densities of krypton and xenon (using an improved form of micro-balance, page 30) were made in 1931 by Whytlaw-Gray and his collaborators. Their results lead to the values for the atomic weight of 83.80 and 131.3 respectively, and these are now the accepted values.

Like argon, these gases are believed to form hydrates, and the isolation of a crystalline hydrate of xenon has been reported.

### § 11 Radon, Thoron or Actinon, Rn, Tn or An

This gas is a product of radioactive decay, is itself radioactive and exists as three isotopes; one in each of the three radioactive series (see Chapter 12, page 163).

It is obtained by dissolving a radium salt in water, when a mixture of oxygen and hydrogen (produced owing to the large amount of energy liberated when radium undergoes radioactive change) and radon is produced. The radon is separated from this mixture by passage through a tube cooled in liquid air, when it is condensed to a liquid.

Radon is used in medicine, in place of radium itself for the treatment of cancerous growths as a number of small samples can be obtained from the same stock of radium. Its period of half-life (3.8 days) although short is sufficient for many purposes.

Radon is only formed in very minute quantities, the largest amount so far obtained pure being 0.0007 mgm. This is in part owing to the small amount of radium (or other radioactive source of the gas) available, and in part to the shortness of its period of average life (see page 162). The density of the gas from radium was determined by Ramsay and Whytlaw-Gray in 1910 by means of the micro-balance and found to be 111.5, corresponding to an atomic weight of 223. Theoretical considerations ( $\alpha$ -ray change from radium, page 141) indicate that its atomic weight should be 222. The present "International" value is 222. The other two isotopes should have atomic weights similarly of 218 and 220, according as they belong to the actinium or thorium series.

### § 12 The Inert Gas Family of Elements

The Inert Gases comprise Group O of the Periodic Table and fall satisfactorily between the very strongly electronegative halogens (Group VIIb) and the strongly electropositive alkali metals (Group Ia). Such properties as they possess exhibit a gradation from member to member as would be expected. Since they form no compounds whose existence has been accepted beyond question (and those which have been reported are extremely few in number) comparison is virtually restricted to the physical properties. The gradation of these is well illustrated by the figures given in Table XXXVIII.

The Inert Gases fall into place very satisfactorily on Lothar Meyer's Atomic Volume Curve, being found just below the alkali metals on the rising portions of the curve (page 129).

In accordance with present views of atomic structure (cf. Chapter 10) the atoms of the Inert Gases have completed groups of 2 or 8 electrons in their outer shells and these are very firmly held comprising a very stable electronic arrangement which is only very slightly affected by changes in the physical conditions to which they are subjected. Consequently, almost linear (or ideal) relationships are found between the

physical properties observed and the atomic numbers or atomic weights. As a further consequence there is no tendency to form ions or ordinary covalent links and therefore there are no compounds of the Inert Gases of these sorts. The only possible way in which compound formation could occur would be by the formation of co-ordinate links in which the Inert Gas atom would be the donor. This could be the explanation of the formation of hydrates and of the compounds of argon with boron trifluoride if their existence is confirmed (*vide supra*). These compounds with few molecules of boron trifluoride would be formed by means of co-ordinate links between argon and boron atoms; the larger molecules would involve co-ordination from fluorine to boron also.

TABLE XXXVIII — PROPERTIES OF THE INERT GASES

Property	Helium	Neon	Argon	Krypton	Xenon	Radon
Atomic No.	2	10	18	36	54	86
Atomic Weight	4.003	20.183	39.944	83.80	131.30	222
Melting Point	-271.4°	-248.7°	-189.2°	-157°	-112°	-71°
Boiling Point	-268.9°	-246.1°	-185.9°	-153.2°	-108.1°	-62°
Critical Temp.	-267.9°	-228.65°	-122.4°	-63.7°	16.7°	104°
Critical Press. (atm.)	2.26	26.86	47.996	54.9	58.22	62
Compressibility ( $\lambda$ , page 112)	-0.00052	-0.00059	-0.0009	0.0028	0.00706	—
Solubility (Vols. in 1 Vol. of water at 0°)	0.0093	0.0104/20°	0.0056	0.0625/20°	0.123/20°	—

## CHAPTER 27

### METALS

#### § 1 General. Occurrence

In an earlier chapter (Chapter 9) the rough classification of the elements into metals and non-metals has been mentioned and reference was made there to some of the characteristic properties of metals. Up to this point in the present work, systematic treatment has concerned only non-metals but the rest of the work will be largely concerned with metals since 68 out of the 90 naturally occurring elements are metals. In addition, metals occupy a commanding position in any civilized economy since not only do the most striking achievements of the civilization of the present day depend upon their use but, in addition, the manufacture of everything we use requires their employment.

Although a few metals such as gold and platinum are found native (that is, in the free or elemental condition), and some other metals occasionally occur free (e.g., copper, silver, iron), the majority have to be extracted from ores which are minerals containing metallic compounds. These minerals are usually mixed intimately with comparatively worthless material so that however they are obtained some degree of concentration of the useful, or elimination of the unwanted, material is necessary before the process of extraction of the metal itself can be undertaken. These processes are sometimes referred to as **mineral beneficiation**.

Table XXXIX gives a list of the principal metals and indicates the nature of their more important ores or minerals. The proportion of useful constituent varies greatly with different samples and the lower limit, below which extraction becomes unprofitable, depends on the nature of the ore and upon the value of the metal concerned. Thus, deposits of galena (the principal ore of lead) can be profitably worked if they contain 5 per cent, or more, of the metal; but ores of tin containing less than 1 per cent have been frequently dealt with and 5 per cent would constitute a rich deposit. Similarly, gold has been successfully extracted from material containing only 3 pennyweights per ton (not quite 0.00005 per cent) and radium is worth winning from a mineral in which it is present to the extent of only 5 mgm. per ton (less than one part in 200 million).

#### § 2 Mineral Beneficiation

The concentration of the valuable constituent of a mineral, so as to obtain a product suitable for the metallurgist to obtain from it a pure metal, is usually carried out in two stages, viz., a preliminary treatment,

TABLE XXXIX — MINERAL OCCURRENCE OF PRINCIPAL METALS

Element	Atomic Number	Native	Oxides	Carbonates	Sulphides	Chlorides	Arsenides	Phosphates	Other Compounds
Lithium	3							Triphylite Amblygonite	Lepidolite (silicate) Spodumene (silicate) Petalite (silicate)
Beryllium	4								Beryl (silicate) Helvite (silicate)
Sodium	11			Iron Natron		Rock Salt			Glauberite (sulphate) Borax (borate) Cryolite (fluoride)
Magnesium	12		Brucite	Dolomite Magnesite		Kamite Carnallite			Epomite (sulphate) Kieserite (sulphate)
Aluminium	13		Corundum Bauxite						Cryolite (fluoride)
Potassium	19					Sylvine Carnallite			Kamite (chloride and sulphate) Schönite (sulphate)
Calcium	20			Chalk Limestone Calcite				Apatite	Fluorspar (fluoride) Gypsum (sulphate)
Vanadium	23								Vanadinite (lead vanadate) Carnotite (uranium vanadate)
Chromium	24		Chromite						
Manganese	25		Manganite Pyrolusite	Rhodocrosite					Rhodonite (silicate)
Iron	26	Iron	Haematite Limonite Magnetite	Chalcite	Pyrite Pyrrhotite			Vivianite	Copperas (sulphate) Ilmenite (titanate)

Cobalt	Zr	Asbolite			Millerite		Chloanthite Kupfernickel		
Nickel	28				Millerite				Garnierite (silicate)
Copper	29	Copper	Azurite Malachite	Cuprite	Chalcopyrite Chalcocite Bornite	Atacamite			
Zinc	30		Calamine	Zincite Franklinite	Zinc Blende				Hemimorphite (silicate)
Molybdenum	42				Molybdenite				Wulfenite (lead molybdate)
Silver	47	Silver			Argentite	Kerargyrite	Proustite		Pyargyrite (antimony sulphide) Stephanite (ditto)
Tin	50			Cassiterite	Stannite				
Tungsten	74								Scheelite (calcium tungstate) Wolframite (iron tungstate)
Platinum	78	Platinum							
Gold	79	Gold							Sylvanite (telluride) Nagavite (lead telluride)
Mercury	80	Mercury			Cinnabar				
Lead	82		Cerussite		Galena	Pyromorphite	Mimetite	Pyromorphite	Vanadinite (vanadate) Wulfenite (molybdate) Crocoisite (chromate) Anglesite (sulphate)
Bismuth	83	Bismuth		Bismuthite	Bismuthine				Tetradymite (telluride)
Uranium	92		Pitchblende						Carnotite (vanadate)

confined to large-size material, in which partial sorting is effected, followed by an after-treatment after grinding or crushing.

### *Preliminary treatment*

In the preliminary treatment the crude mineral is reduced in size to lumps of between four inches and six inches in diameter, if larger than this, and any adhering material, or mud, washed off with sprays of water. The lumps are then fed on to a moving belt and, where possible, the lumps of unwanted rock are picked off by hand. The remainder is then further crushed to the size of gravel and finally fed to a stamping mill, or ball mill, for conversion to "sand" or "slime" for after-treatment.

### *After-treatment*

There are three main types of after-treatment. These are:

- (1) Methods depending upon differences of specific gravity, such as:
  - (a) mechanical washing with water;
  - (b) dense medium separation (for which a medium is chosen in which the less dense constituents of the ore will float and the denser ones will sink).
- (2) Methods depending upon the chemical composition of the mineral, e.g.:
  - (a) The flotation process;
  - (b) solution methods.
- (3) Methods depending upon electrical or magnetic characteristics, such as:
  - (a) magnetic separation;
  - (b) electrostatic precipitation.

As an example of the use of methods 1(a) and (b) the concentration of galena (mainly lead sulphide) occurring in limestone may be quoted. Thus, in a running stream of water the particles of galena sink to the bottom whilst the less dense limestone is carried away. Similarly, in a suitable dense liquid limestone (sp. gr. c. 2.5) would float while galena (sp. gr. c. 7.5) would sink.

Flotation methods 2(a) are widely used. A good example of their use is the separation of galena and zinc blende (chiefly zinc sulphide) from the quartz and felspar with which they are often associated. For this purpose a small amount of potassium cyanide and of slaked lime is mixed with the mineral being crushed in the ball mill, from which it emerges in the form of a slurry, or pulp, with water. Pine oil, or cresylic acid, and a very small, carefully regulated quantity of potassium xanthate (potassium dithiocarbonate,  $K_2COS_2$ ) are then added and the whole is agitated by means of air until a froth is formed.

The potassium cyanide and the slaked lime exert a selective action



on the surface of the zinc blende so that when the pine oil and potassium xanthate are added only the galena is carried over in the froth. After the removal of the galena in this way, a little copper sulphate is added to the residue followed by further small quantities of pine oil and potassium xanthate. Further agitation by air now creates a froth which contains zinc blende which is carried over and so separated from felspar, quartz and other materials which are unaffected by any of the substances added. This method is found to be most successful with sulphide minerals; oxides, carbonates or silicates give less satisfactory results.

The extraction of gold (page 674) is a good example of the use of a solution method 2(b); magnetic separation is used for the removal of wolframite (the principal ore of tungsten) from tin concentrates (page 879).

### § 3 Extraction of Metals from their Ores

The methods employed for the extraction of metals from the concentrated ores, in a more or less pure condition, may be summarized as follows:

- (1) Reduction of the oxide with hydrogen (e.g., tungsten).
- (2) Reduction of the oxide with carbon or carbon monoxide (e.g., iron, zinc, tin).
- (3) Reduction of the oxide with aluminium (thermite process, e.g., chromium, manganese).
- (4) Oxidation (autoreduction) of the sulphide (e.g., copper, lead, mercury).
- (5) Reduction of the sulphide with iron (e.g., antimony).
- (6) Electrolytic processes (e.g., sodium, magnesium, calcium, aluminium).
- (7) Special methods (e.g., cyanide extraction of silver, carbon monoxide for nickel).

The choice of process in any particular instance depends upon the chemical nature of the ore and the properties of the metal concerned. It may be noted that a great many workable metallic ores are sulphides, whereas suitable extraction methods may involve the reduction of the oxide. In such cases (as also when the ore is a carbonate) a preliminary roasting is necessary in order to convert the ore into the oxide. (Cf. the extraction of zinc, page 715.) This preliminary roasting is also necessary for the production of the proportion of oxide required for autoreduction methods. (Cf. lead, page 792.)

In recent years the use of solvent extraction methods at elevated temperatures and pressures has been much investigated and applied to the production of a number of metals. These methods have become known as the Forward process from the name of one of their principal investigators and are being applied, for example, to the extraction of copper, nickel and uranium.

### § 4 Properties of Metals

Some of the more obvious properties of metals have been mentioned already in Chapter 9. Thus, they are good conductors of heat and electricity, they are opaque to light (except in very thin layers) and they are very good reflectors. Many metals also emit electrons when heated. These properties are explained by the presence of free electrons. All metals are crystalline, although this is not obvious since the geometrical boundaries of the crystals are not often observed. But they are constructed from simple space-lattices (page 196) in which the structural units are the ions of the metal and free electrons are contained in the crystal in some way which is not yet completely understood.

At the same time metals exhibit other properties, such as hardness, melting point, thermal expansion and compressibility, which show large variations from one metal to another. Thus, while the melting point of mercury is  $-39^{\circ}\text{C.}$ , that of tungsten is  $3300^{\circ}\text{C.}$ , while coefficients of thermal expansion and of compressibility likewise vary enormously. These properties depend upon the differences between the crystal structures concerned and not, like the former ones, on some one constant factor such as the presence of free electrons.

As regards their chemical activity, metals similarly show wide divergences ranging from the extremely reactive alkali metals to the almost inert platinum group. In this respect, metals can be arranged in a series in order of their chemical reactivity which is the same as the order of the electrochemical series as has been mentioned above (page 231).

The most active metals will liberate hydrogen from water. Many of them (e.g., the alkali metals and the metals of the alkaline earths) will do so at ordinary temperatures; others, such as magnesium and zinc, will react thus with steam at  $100^{\circ}\text{C.}$  Iron and steam react at a red heat; manganese and cobalt behave similarly. Metals below hydrogen in the electrochemical series do not liberate hydrogen from water.

Many metals also liberate hydrogen from dilute mineral acids in the cold: in particular from dilute hydrochloric or sulphuric acid. Nitric acid usually yields oxides of nitrogen and not hydrogen, although magnesium and manganese can set free the latter gas with very dilute acid and under carefully controlled conditions. (Cf. page 689.) Again, metals below hydrogen in the electrochemical series do not behave in this way.

The behaviour of metals towards oxygen is parallel to that with water and acids. At ordinary temperatures gold and platinum are unaffected; other metals, like copper, lead, tin, iron, chromium or aluminium, are slowly oxidized on the surface, but, since the film of oxide formed is continuous and the rate at which gases diffuse through it is very slow, further oxidation soon ceases. With metals like zinc, magnesium or calcium a discontinuous oxide film results so that oxidation continues at the initial rate although this may be quite slow.

As with all chemical reactions the rate at which these processes occur increases with temperature so that the initial oxide films are formed more rapidly. If the oxide layer is discontinuous (as with magnesium or zinc) the metal undergoes rapid oxidation at high temperatures. Where continuous films are formed the initial rate of oxidation will again increase with rise of temperature but the extent to which oxidation will proceed in a given time will depend upon the rate of diffusion of oxygen through the oxide layer. On aluminium or chromium, for example, the oxide layer remains very resistant to diffusion so that the initial film, though formed more rapidly at higher temperatures, thickens very slowly, if at all. On other metals, such as copper and iron, the rate of diffusion increases considerably with rise of temperature and so the layer of oxide must become much thicker before the rate at which oxygen can reach fresh metal becomes negligible. With increasing thickness the tendency of the oxide layer to crack becomes greater and this, in turn, increases the rate of attack. Resistance to oxidation, at high temperatures, thus occurs only when the oxide layer first formed becomes impervious to oxygen while it is still quite thin.

The action of oxygen on molten metals will differ according to whether the oxide formed dissolves in the metal, as it does in the case of copper, or remains as a surface layer (or scum) as with aluminium or tin.

Some of the results of the action of pure oxygen on metals are much modified, when the effect of exposure to the atmosphere is under consideration, owing to the presence of other gases and of water vapour. (Cf. corrosion of iron, page 916; patina on copper, page 650.)

### § 5 Oxides and Hydroxides of Metals

Oxygen combines with all the metals forming oxides, and almost all metals also form hydroxides; the principal exception is silver

The methods available for the preparation of metallic oxides are:

- (i) burning the metal in air as oxygen, e.g.,  $\text{Na}_2\text{O}_2$ ;
- (ii) burning the metal in steam, e.g.,  $\text{MgO}$ ,  $\text{ZnO}$ ;
- (iii) action of steam on the red-hot metal, e.g.,  $\text{Fe}_3\text{O}_4$ ;
- (iv) decomposition of the hydroxide by heat, e.g.,  $\text{CuO}$ ;
- (v) decomposition of the carbonate by heat, e.g.,  $\text{CaO}$ ;
- (vi) decomposition of the nitrate by heat, e.g.,  $\text{PbO}$ ;
- (vii) decomposition of a compound (or saline) oxide, e.g.,  $\text{PbO}_2$ .

Metallic oxides are insoluble in water; those which appear to dissolve (such as sodium monoxide, or calcium oxide) react with the water first to form the corresponding hydroxides, which are soluble.

Metallic hydroxides can be obtained by the action of:

- (i) water on the metal, e.g.,  $\text{NaOH}$ ,  $\text{KOH}$ ;
- (ii) water on the oxide, e.g.,  $\text{Ca(OH)}_2$ ;

- (iii) sodium hydroxide solution on a solution of a salt of the metal, e.g.,  $\text{Cu}(\text{OH})_2$ ;
- (iv) milk of lime on a solution of a carbonate, e.g.,  $\text{NaOH}$ ;
- (v) sodium carbonate solution on a solution of a salt of the metal, e.g.,  $\text{Sn}(\text{OH})_4$ ;
- (vi) ammonia solution on a solution of a salt of the metal, e.g.,  $\text{Fe}(\text{OH})_3$ ;
- (vii) heat on the carbonate in presence of superheated steam, e.g.,  $\text{Ba}(\text{OH})_2$ ;
- (viii) chlorine on an alkaline suspension of a lower oxide or hydroxide, e.g.,  $\text{Ni}(\text{OH})_2$ .

The choice of method is determined, as in the preparation of oxides, by the properties of the compound being made.

Metallic hydroxides are mostly insoluble in water: the exceptions are those of the alkali metals, which are extremely soluble, and of the alkaline earth metals, which are sparingly soluble. Only the hydroxides of the alkali metals can be heated without change; the others all lose water, becoming converted into oxides (or, in the case of noble metals, the metal itself).

### § 6 Metallic Carbonates

Most metals (except those, like aluminium, whose hydroxides are very weak bases) form carbonates. These can be obtained by:

- (i) precipitation from solutions of salts of the metal by (a) sodium carbonate solution, e.g.,  $\text{CuCO}_3$ , or (b) sodium bicarbonate solution, e.g.,  $\text{ZnCO}_3$ ;
- (ii) passing carbon dioxide through a solution of the hydroxide, e.g.,  $\text{CaCO}_3$ ;
- (iii) decomposition of the bicarbonate by heat, e.g.,  $\text{Na}_2\text{CO}_3$ .

Many metals also form basic carbonates (e.g., magnesium, calcium and lead). Some of these are important articles of commerce (e.g., white lead).

The only carbonates which are soluble in water are those of the alkali metals but some bicarbonates are readily soluble in presence of excess of carbon dioxide. Thallous carbonate, also, is fairly soluble. (The part played by the solubility of the bicarbonates of magnesium and calcium in the phenomenon of the hardness of water has been discussed on page 308.) All carbonates, except those of the alkali metals, are decomposed by heat yielding the oxide and carbon dioxide. The metallic bicarbonates are similarly unstable to heat.

### § 7 Metallic Chlorides, Nitrates, Sulphides and Sulphates

#### Chlorides

Chlorides of all the metals are known and can be prepared by one or more of the following methods:

- (i) direct combination of the metal with chlorine, e.g.,  $\text{AlCl}_3$ ;
- (ii) the action of hydrogen chloride on the heated metal, e.g.,  $\text{FeCl}_2$ ;
- (iii) the action of hydrochloric acid on (a) the metal, e.g.,  $\text{SnCl}_2$ , or (b) the oxide, e.g.,  $\text{CoCl}_2$ , or (c) the hydroxide, e.g.,  $\text{CuCl}_2$ , or (d) the carbonate, e.g.,  $\text{CaCl}_2$ ;
- (iv) the action of aqua regia on the metal, e.g.,  $\text{AuCl}_3$ ,  $\text{PtCl}_4$ ;
- (v) the reduction of a higher chloride, e.g.,  $\text{Hg}_2\text{Cl}_2$ ;
- (vi) precipitation from a solution of a soluble salt, e.g.,  $\text{AgCl}$ .

Almost all metallic chlorides are soluble in water, exceptions being silver, aurous, mercurous, thalious, cuprous, and palladous chlorides, white lead chloride, which is sparingly soluble in cold water, is soluble in hot. The chlorides, except those of the noble metals, are stable to heat.

### Nitrates

Most metals, apart from some of the noble metals, form nitrates and these salts can be prepared by suitable methods from the following list:

- (i) the action of nitric acid on (a) the metal, e.g.,  $\text{Cu}(\text{NO}_3)_2$ , or (b) the oxide, e.g.,  $\text{Pb}(\text{NO}_3)_2$ , or (c) the hydroxide, e.g.,  $\text{NaNO}_3$ , or (d) the carbonate, e.g.,  $\text{Ba}(\text{NO}_3)_2$ ;
- (ii) the action of sodium nitrate on the corresponding chloride, e.g.,  $\text{KNO}_3$ .

All nitrates are soluble in water and all undergo some decomposition when heated. The nitrates of the alkali metals lose oxygen and are so converted into the corresponding nitrites (page 628); those of the heavy metals lose nitrogen peroxide and oxygen leaving the oxide; silver nitrate is converted into the metal itself and ammonium nitrate is decomposed into nitrous oxide and water (page 457).

### Sulphides

A great many metals occur naturally as sulphides (cf. Table XXXIX). These sulphides can also be prepared in the laboratory by the following methods, viz.:

- (i) the direct combination of the metal with sulphur (usually on heating), e.g.,  $\text{FeS}$ ;
- (ii) the action of hydrogen sulphide on aqueous solutions of soluble salts of the metal concerned, e.g.,  $\text{CuS}$ ;
- (iii) reduction of the sulphate with carbon, e.g.,  $\text{BaS}$ ;
- (iv) heating a mixture of the oxide with carbon and sulphur, e.g.,  $\text{Al}_2\text{S}_3$ .

Many sulphides are soluble in water, e.g., those of the alkali metals; those of the heavy metals are mostly insoluble. Sulphides, on heating in

air, are usually oxidized to the metallic oxide and sulphur dioxide; this is a reaction which is important in metallurgy (*vide supra*). In the absence of air sulphides are usually stable when heated.

### Sulphates

Sulphates of most metals can be obtained by the usual methods for preparing salts, such as:

- (i) the action of dilute sulphuric acid on (a) the metal, e.g.,  $\text{FeSO}_4$ , or (b) the oxide, e.g.,  $\text{CuSO}_4$ , or (c) the hydroxide, e.g.,  $\text{Al}_2(\text{SO}_4)_3$ , or (d) the carbonate, e.g.,  $\text{ZnSO}_4$ ;
- (ii) precipitation by addition of dilute sulphuric acid or a soluble sulphate to a soluble salt of the metal, e.g.,  $\text{PbSO}_4$ ;
- (iii) the action of hot, concentrated sulphuric acid on a salt of a more volatile acid, e.g.,  $\text{Na}_2\text{SO}_4$  from  $\text{NaCl}$  or  $\text{NaNO}_3$ .

Most metallic sulphates are soluble in water: the sulphates of lead, calcium, strontium and barium are the principal exceptions. The sulphates are also stable when heated.

## CHAPTER 28

# THE ALKALI METALS

Potash is both wealth and weapon. Our position as sole producer gives us the power of causing grave injury to the agriculture of our enemies by stopping the export of salts so indispensable to them for manurial purposes. If raw materials are refused us, we shall revenge ourselves on the enemy's agriculture with this war cry: "At the enemy with a kilo of potash!"—*Vossische Zeitung* (November 23rd, 1917).

### § 1 Group I of the Periodic Table

GROUP I of the Periodic Table comprises eight elements, arranged in two sub-groups, viz., lithium, sodium, potassium, rubidium and caesium in the A sub-group; whilst copper, silver and gold constitute the B sub-group. As usual at the extreme ends of the table, the relationship between the elements in the two sub-groups is not very marked, but each sub-group forms a family of elements—the A sub-group being very well defined; the B sub-group rather less so.

This is well seen in the properties of the elements of Group IA which are known as the alkali metals.

This behaviour is to be expected from the electronic structure of the atoms of these elements. The alkali metals have a single electron in the outermost group, the rest of the atom having the very stable Inert Gas configuration, whereas in copper, silver and gold the penultimate group consists of 18 electrons, a much less stable arrangement than the 8 of the Inert Gases. This group of 18 can lose electrons under suitable conditions thus giving rise to valencies greater than one in these elements.

The gradation of properties in both sub-groups and discussion in terms of the structures of the atoms of these elements are considered more fully at the end of Chapter 29 (page 679). It may be noted here, however, that the alkali metals, having a single electron in the outermost group, are characterized by being very strongly electropositive and persistently monovalent: the tendency to form an electropositive monovalent ion by loss of one electron is very marked indeed.

### § 2 Lithium, Li

#### History and Occurrence

Lithium was discovered by Arfvedson in 1817 during the course of an analysis of the metal petalite. The name lithium (from *λίθος*, *litheos*—stony) was given to it because it was then believed to be confined to the mineral kingdom. The metal was isolated in 1855 by Bunsen and Matthiessen by electrolysis of the fused chloride.

Lithium is a rare, but widely distributed, element. It occurs in a number of minerals, e.g., in *lepidolite* or lithia mica, which contains up to 6 per cent of

lithia as lithium aluminium fluosilicate; *spodumene*, a lithium aluminium silicate— $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ —contains a similar amount, while *amblygonite*,  $\text{Li}(\text{AlF})\text{PO}_4$ , and *petalite*—a lithium sodium aluminosilicate—contain 7 to 10 per cent and 3 per cent respectively. Lithium has been detected in the ash of many plants, notably tobacco; in milk, blood and in many mineral springs.

### Preparation

The principal minerals from which lithium and its compounds are obtained commercially are spodumene, lepidolite and amblygonite.

Various methods have been employed for the extraction of lithium compounds from these minerals. They depend ultimately either upon the sparing solubility of lithium carbonate as compared with the other alkali metals, or upon the solubility of lithium chloride in alcohol (sodium and potassium chlorides being insoluble).

The phosphates such as amblygonite are readily decomposed by acids, but the silicates react much less readily. One method used with the silicate minerals is to heat them to redness, when finely ground, with excess of potassium sulphate. The aqueous extract of the cooled product then contains lithium sulphate from which lithium carbonate is precipitated by addition of potassium or ammonium carbonate.

In another process, the powdered mineral is fused with a mixture of barium carbonate, barium sulphate and potassium sulphate. Two layers result—the upper, consisting of lithium and potassium sulphates, is dissolved in water, treated with barium chloride and the lithium chloride extracted as before.

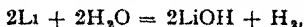
The metal is readily made by electrolysis of the fused chloride, using a carbon anode and an iron cathode, and its production in this way is being undertaken technically now that uses of the element are becoming more numerous (page 609).

### Properties

Lithium is a silvery white metal resembling sodium and potassium in appearance, but harder than they are, and with a higher melting point, viz.,  $186^\circ$ . It boils at  $1380^\circ$ . It has a density of only 0.534, which is lower than that of any other solid element at ordinary temperatures. It is fairly volatile, and its vapour imparts a carmine-red colour to a bunsen flame. It has the highest specific heat (0.96 at  $50^\circ$ ) of any element.

Although chemically an active element, lithium is the least active of the alkali metals. It burns in air with a brilliant white light resembling that of burning magnesium, forming the monoxide  $\text{Li}_2\text{O}$ ; it does not readily form a higher oxide. It combines readily with hydrogen at a red heat, forming the hydride  $\text{LiH}$ , and also easily forms a nitride,  $\text{Li}_3\text{N}$ , by combination with nitrogen. It also combines directly with the halogens and sulphur.

Lithium reacts with water, forming the hydroxide and hydrogen,



but the hydrogen does not catch fire even if the water be boiling; neither does the metal melt. As a strongly electropositive element it reacts vigorously with acids.

The atomic weight of lithium was determined by Richards by conversion of lithium chloride to lithium perchlorate, and to silver chloride. His value, 6.94, is that at present accepted.

## § 3 Lithium Hydride, Oxides and Hydroxide

Lithium hydride,  $\text{LiH}$ , formed by direct combination of the elements, is noteworthy in that electrolysis of the fused compound furnishes hydrogen at the anode. When acted upon by water it gives off hydrogen, with evolution of a considerable amount of heat.



**Lithium aluminium hydride**,  $\text{LiAlH}_4$ , is used as a reducing agent in organic chemistry (page 747).

**Lithium oxide**,  $\text{Li}_2\text{O}$ , can be made by heating the metal in air or, more satisfactorily, by heating the hydroxide to redness in an atmosphere of dry hydrogen. Lithium oxide is a white powder which reacts slowly with water, forming a solution of the hydroxide. The reaction mentioned above is thus reversible:



**Lithium peroxide**,  $\text{Li}_2\text{O}_2$ , is obtained as a double compound with hydrogen peroxide by the action of hydrogen peroxide on lithium hydroxide:



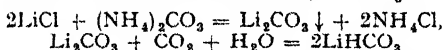
This can be dehydrated by keeping over phosphorus pentoxide.

**Lithium hydroxide**,  $\text{LiOH}$ , is made by the action of water on the free metal, and is a white crystalline substance rather resembling sodium hydroxide, but less readily soluble in water. It can also be prepared by addition of baryta water to a solution of lithium sulphate.

**Lithium nitride**,  $\text{Li}_3\text{N}$ , is formed by the direct combination of lithium and nitrogen, which takes place readily; slowly even at room temperature

## § 4 Salts of Lithium

**Lithium carbonate**,  $\text{Li}_2\text{CO}_3$ , is precipitated as a white solid by the addition of ammonium carbonate solution to a solution of a soluble lithium salt. It is noteworthy in being thus sparingly soluble (100 grams of water dissolve 1.54 grams at  $0^\circ\text{C}$ . and 1.38 grams at  $15^\circ$ ); for the carbonates of the other alkali metals are all soluble. Further, like the insoluble carbonates of the alkaline earths (Chapter 30, pages 691, 701), it is soluble in presence of excess of carbon dioxide on account of the formation of a soluble **lithium bicarbonate**,  $\text{LiHCO}_3$ .



The solution of the bicarbonate is sold and used medicinally under the name *lithia water*. The normal carbonate, when heated to about  $800^\circ$  in an atmosphere of hydrogen, decomposes into the oxide and carbon dioxide:



**Lithium chloride**,  $\text{LiCl}$ , is the salt of lithium usually prepared when the element is being extracted from minerals containing it. In general behaviour, etc., it is similar to sodium chloride, but its solubility in water is much greater and it is very deliquescent, being perhaps the most deliquescent substance known.

Of the remaining halides, the **fluoride** is notable for its very sparing solubility in water—in this again lithium resembles the alkaline earths. The **nitrate** is a very deliquescent salt and, like the chloride and sulphate, is soluble in alcohol.

**Lithium sulphate** crystallizes from water, in which it is readily soluble, with one molecule of water of crystallization— $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ .

**Lithium (ortho) phosphate**,  $\text{Li}_3\text{PO}_4$ , like the carbonate, is virtually insoluble and is precipitated when sodium phosphate solution is added to a solution of a soluble lithium salt such as the chloride. This again shows the similarity of lithium to the elements of the alkaline earth group.

## § 5 Uses of Lithium and Lithium Compounds

Until comparatively recently lithium and its compounds had little use either industrially or in the laboratory, almost the only employment usually mentioned being the use of lithium salts in the treatment of diseases such as gout caused by uric acid; its use for this purpose being suggested by the fact that lithium urate is one of the very few soluble salts of uric acid.

Of late, however, there has been considerable expansion in the manufacture and use of lithium and lithium salts. Thus it is used in the form of an alloy of lead for bearings; it is used to improve the tensile strength and resistance to corrosion of aluminium alloys, and an alloy of zinc and aluminium, containing in addition about 0.1 per cent of lithium, possesses elasticity and tensile strength of a similar order to that of mild steel. Calcium-lithium alloys are used for the purification of copper for purposes where a metal of very high conductivity is required; copper-lithium alloys are also used to "modify" the graphite in "high-duty" cast iron (inoculation process). Ten per cent of lithium hydroxide is often added to the potassium hydroxide used for the electrolyte of nickel-iron accumulators. Lithium chloride solutions have been used in air-condition plant for regulating the humidity of the air, and lithium compounds are now employed in the manufacture of glasses and glazes.

### § 6 Detection and Determination of Lithium Compounds

Lithium is detected by means of the red coloration it imparts to the bunsen flame, when examined spectroscopically, this flame is seen to give a faint yellow line of slightly longer wave-length than the D lines of sodium, and a brilliant crimson line. Lithium is also recognized by the precipitation of its insoluble phosphate on the addition of sodium phosphate, a process which is also sometimes employed for its determination. The use of the fluoride has similarly been suggested. It is usual to determine it as sulphate, like sodium (q.v.), and to separate it from the other alkali metals by extraction with amyl alcohol.

### § 7 Sodium, Na. History and Occurrence

Sodium chloride, or common salt, and sodium carbonate have been known since very early times; for the former is probably a vital necessity and has certainly been employed in food for an indefinitely long period, whilst the latter, which comprises a considerable proportion of the ashes of maritime plants, also occurs native and was known to, and employed by, the ancient Egyptians.

Metallic sodium was first obtained by Sir H. Davy in 1807 by electrolysis of fused caustic soda.

Sodium, in the form of compounds, is a widely distributed and abundant element, but on account of its intense chemical activity is never found free.

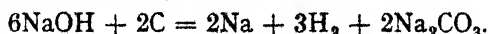
Sodium chloride occurs in enormous quantities in the sea, and is also found in extensive deposits of rock salt, presumably formed as a result of the evaporation of prehistoric seas. Rock salt is found at Northwich and Middlewich in Cheshire, Droitwich\* in Worcestershire, Preesall in Lancashire, Middlesbrough in Yorkshire, Stassfurt in Saxony, Cardona and Castile in Spain, California, Kansas, Utah, New York, Virginia, Ohio and Michigan in the U.S.A., and numerous other places. The salt mine at Wielicza in Galicia has been worked continuously for 600 years. The salt deposit there is said to be 500 miles long, 20 miles wide and 1200 feet thick. Another vast potential source of salt is the Salt Range of the Punjab. Salt was first noticed in this region by Strabo (first century).

\* The names of these places indicate the antiquity of the salt industry since the Saxon name for a place where natural brine was boiled was "wich."

Sodium also occurs in large quantities in the form of complex aluminosilicates, such as *soda-felspar* (page 765); and the weathering of rocks and minerals of this type has given rise to sodium carbonate and clay. Much of the sodium carbonate is found in inland seas, etc., but considerable deposits exist, known as *trona*,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , in Egypt and other places. Large deposits of borax (sodium diborate) are also found, e.g., in Nevada (U.S.A.), and the Chile nitrate beds are largely composed of sodium compounds.

### § 8 Manufacture of Metallic Sodium

Metallic sodium was for many years manufactured by a process developed by Castner in which caustic soda was heated with a mixture of carbon and iron at a temperature of  $1000^\circ$ .



This method was later superseded by the electrolysis of fused caustic soda, the type of plant employed being also devised by Castner. This, in its turn, has now been replaced by the electrolysis of fused sodium chloride.

The manufacture of sodium directly by the electrolysis of fused common salt, is attended with considerable difficulties, owing to the high melting point of salt, but these difficulties have now been overcome. The Downs cell, used for this purpose, is shown diagrammatically in Fig. 28.1. In it there is a central graphite anode *A* screened from an annular cast steel cathode *B* by an iron gauze diaphragm *C*. Surmounting the anode is a conical hood *D* through which the chlorine evolved is led off and over the cathode is an inverted circular trough *E* into which the sodium rises and from which it is led off. The electrolyte consists of a fused mixture of common salt and calcium chloride, or sodium fluoride, which melts at about  $600^\circ$  (common salt itself melts at about  $800^\circ$ ). The cell itself consists of an outer iron shell lined with firebrick.

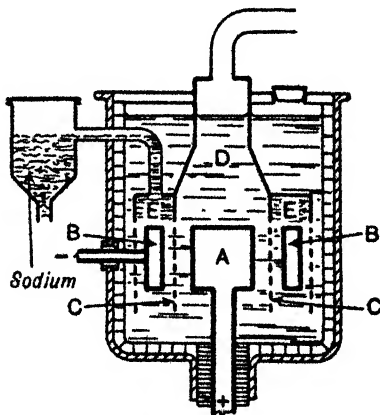


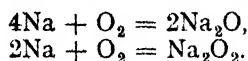
FIG 28.1 —Downs Cell

### § 9 Properties of Sodium

Sodium is a silvery-white, lustrous metal which tarnishes at once when exposed to the air, owing to the formation of a film of oxide. On account of the ease with which it is oxidized (see below), it must

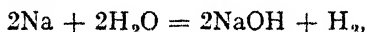
be kept immersed in a liquid containing no oxygen. It is less dense than water (sp. gr. 0.93); it is soft, so that it can be cut with a knife, and at ordinary temperatures can be moulded between the fingers. Sodium melts at  $97.7^{\circ}$ , and boils at  $883^{\circ}$ . The vapour, which is purple when seen in thick layers, has a density of 12.85 ( $H_2 = 1$ ) indicating that it is probably almost entirely monatomic. Sodium is a good conductor of electricity.

Chemically, sodium is a very reactive element. It combines vigorously with oxygen, burning readily in air with a brilliant yellow flame, and forming a mixture of the oxide and peroxide:

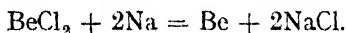


It combines directly with the halogens and with phosphorus, taking fire when heated with these elements. It also combines with hydrogen when heated to  $360^{\circ}$ .

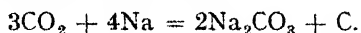
The vigour of its combination with oxygen is such that sodium will react with most oxides, liberating the element previously combined with the oxygen. Thus, it acts energetically with water, forming sodium hydroxide and hydrogen,



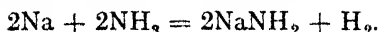
and the heat of the reaction is sufficient to melt the sodium, which swims about as a globule on the surface of the water. The heat evolved is, however, not great enough to ignite the hydrogen unless large pieces of sodium are used, or the water is warmed, or the movement of the sodium is prevented. With the oxides of most metals, the metal itself is formed. A similar reaction takes place with metallic chlorides and has been applied to the preparation of metals such as beryllium and uranium, etc.:



Aluminium also was formerly prepared in this way. Non-metallic oxides are similarly reduced. Thus sodium will burn in carbon dioxide forming carbon and sodium carbonate:



Sodium will dissolve in liquid ammonia forming a blue solution, but when heated in ammonia gas sodamide results:



It also dissolves in mercury, forming sodium amalgam (page 725) and reacts violently with acids.

## § 10 Uses of Sodium

Sodium is used in the manufacture of sodium peroxide, sodium cyanide and sodamide, all of which (particularly the two last-named) are of technical importance. The metal is employed as a reagent in organic

chemistry, and an alloy with potassium, which is liquid at ordinary temperatures, is employed in high-temperature thermometers. It was formerly used in the manufacture of aluminium and magnesium, but these are now made by electrolysis (pages 687, 743). The possibility of using sodium in the production of very light alloys for aircraft is now being investigated, and its alloy with lead is used in large quantities in the manufacture of lead tetraethyl (the so-called "ethyl-fluid" of commerce) for making anti-knock motor spirit. Sodium is now also used for the modification of casting alloys of aluminium and silicon: the addition of as little as 0.05 per cent of sodium to the molten alloy results in considerable enhancement of the physical properties of the alloys. It is employed for the cooling of the valves of aero-engines (the valve being hollow and partially filled with sodium) on account of its efficiency as a heat-transfer medium.

Sodium is also likely to find increasing use, in the future, for heat transfer in nuclear reactors. Like all the alkali metals, sodium exhibits the photo-electric effect (i.e., emission of electrons when exposed to light) in marked degree and hence is used widely for the photo-electric cells on which television, the telegraphic transmission of pictures, the talking-film and many other modern devices depend.

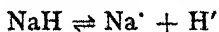
### § 11 Atomic Weight of Sodium

That the atomic weight of sodium lies in the neighbourhood of 23 is indicated by its specific heat (0.283) which, by Dulong and Petit's rule (page 98), gives 22.6 for the atomic weight. There is much evidence also that it is monovalent (e.g., molecular weight of some of its salts in solution in various solvents) and the equivalent weight is also found to be close to 23.

The best chemical determinations are probably those of Richards and Wells. By conversion of very pure sodium chloride into silver chloride they determined the ratios  $\text{AgCl}/\text{NaCl}$  and  $\text{Ag}/\text{NaCl}$  leading to the values 22.995 and 22.998 respectively for the atomic weight of sodium. The value at present adopted by the International Committee is 22.991 based on mass spectrograph measurements and nuclear calculations.

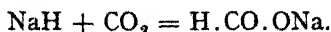
### § 12 Hydride and Oxides of Sodium

**Sodium hydride**,  $\text{NaH}$ , is prepared by passing dry hydrogen over sodium at about  $360^\circ$ . It is decomposed by water with evolution of hydrogen; and on heating, the colourless crystals of the hydride dissociate into their elements. As with lithium hydride, when subjected to electrolysis, hydrogen is evolved at the **anode** showing that hydrogen can, in these circumstances, form a *negatively* charged ion:



whereas normally it forms a positive ion. Sodium hydride combines

with carbon dioxide, forming sodium formate (the sodium salt of the organic acid formic acid):



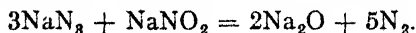
### Oxides of Sodium

Sodium forms three well-defined oxides, viz.:

Sodium monoxide,  $\text{Na}_2\text{O}$ ,  
Sodium peroxide,  $\text{Na}_2\text{O}_2$ ,  
Sodium dioxide,  $\text{NaO}_2$ .

A fourth oxide,  $\text{Na}_2\text{O}_3$ , obtained by passing oxygen into a solution of sodium in liquid ammonia has also been reported.

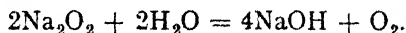
**Sodium monoxide**,  $\text{Na}_2\text{O}$ , is formed, along with the peroxide, when sodium is burned in air or oxygen. It is difficult to obtain pure in this way, even when a limited supply of air is used, and is better made by heating sodium azide with sodium nitrate or nitrite:



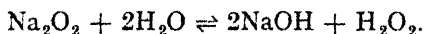
It is a white solid which combines with water with the evolution of much heat, forming sodium hydroxide.

**Sodium peroxide**,  $\text{Na}_2\text{O}_2$ , is formed when sodium is burned in oxygen or (along with the monoxide) in air. It is made commercially by passing excess of dry air, free from carbon dioxide, over sodium contained in aluminium trays in iron tubes heated to about  $300^\circ$ . The product contains about 95 per cent of sodium peroxide and is usually slightly yellow, although the pure compound is white.

Sodium peroxide is not decomposed by heat and is stable in dry air; but in moist air, or when acted upon by water, it is decomposed with evolution of oxygen and formation of sodium hydroxide:



If the temperature be kept low, however, water yields hydrogen peroxide, a reaction which is found to be reversible, since a hydrated sodium peroxide,  $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ , crystallizes out when hydrogen peroxide is added to a cold concentrated solution of sodium hydroxide:



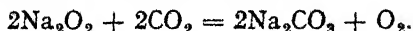
Hydrogen peroxide is also formed by the action of acids in the cold.

Sodium peroxide is a powerful oxidizing agent, and is used in the laboratory for oxidizing purposes, e.g., in qualitative analysis to convert chromic hydroxide into sodium chromate, and also for decomposing silicate rocks prior to analysis. It combines with carbon monoxide, forming sodium carbonate:



and also reacts with carbon dioxide, which it absorbs with liberation

of oxygen. It is thus used for the revivification of air which has been vitiated in breathing (e.g., in submarines):



Sodium peroxide also oxidizes sulphides to sulphates when fused with them, a process often made use of for the estimation of such sulphides, and ammonia to nitrogen.

In addition to the above uses, sodium peroxide is also used for the bleaching of textiles; for the manufacture of benzoyl peroxide used for bleaching flour; for the production of calcium peroxide used for the activation of yeast; in the manufacture of sodium perborate (page 741), and in the production of dyes and other synthetic organic chemicals.

**Sodium dioxide,  $\text{NaO}_2$ .** It has recently been shown by George (1955) that commercial sodium peroxide contains 10 per cent of sodium dioxide. It can be obtained in high yield by heating sodium peroxide in oxygen at  $490^\circ$  and at 298 atmospheres pressure. It reacts with water to give hydrogen peroxide, oxygen and sodium hydroxide



It is probably the cause of the pale yellow colour of commercial sodium peroxide.

### § 13 Sodium Hydroxide, Caustic Soda, $\text{NaOH}$

Sodium hydroxide is a very important industrial heavy chemical and is manufactured on a large scale. It can be prepared:

- (i) by the action of sodium on water;
- (ii) by the action of milk of lime on sodium carbonate solution;
- (iii) by the electrolysis of solutions of sodium chloride.

The first of these methods is only used for the preparation of small quantities of specially pure sodium hydroxide for use in the laboratory; both the remaining methods are employed extensively in industry.

#### Manufacture of Caustic Soda from Sodium Carbonate

This process depends upon the fact that when milk of lime is boiled with a solution of sodium carbonate, calcium carbonate is precipitated and sodium hydroxide remains in solution:

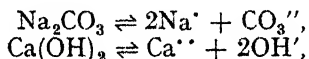


It is known as *causticization* and is carried out industrially in large iron tanks, having a mechanical stirring apparatus and an inlet for a supply of steam. A solution of commercial sodium carbonate is run in and quicklime is placed in an iron cage dipping into the solution. The mixture is agitated by means of the stirrer and also by steam, which is blown into the solution to heat it. The sodium carbonate is largely converted into caustic soda, calcium carbonate being precipitated.

The mixture was formerly run into settling tanks, and after the precipitated calcium carbonate had settled, the clear liquid was run off and concentrated. The sludge remaining contained a considerable proportion of caustic soda which represented so much loss; but the prevention of this loss by filtering off the calcium carbonate was formerly impracticable owing to the properties of the caustic soda solution. Latterly, however, the use of plant made of monel metal has made this possible and the causticized liquor is filtered off under reduced pressure and evaporated in multiple-stage vacuum evaporators heated by steam. Concentration beyond a certain point is not practicable with steam heating and the final stage is effected by heating the concentrated liquor in cast-iron vessels set in brickwork over a free fire until all the water has been driven off and fused caustic soda is left.

The reaction between sodium carbonate and slaked lime is reversible and is never complete, but equilibrium is found to be more over to the calcium carbonate side of the equation the more dilute the solution is as a whole.

These facts are explained on the basis of the Ionic Theory as follows. At the start we have the equilibria



so that the solution contains sodium, calcium, carbonate and hydroxyl ions. The solubility product (page 262) of calcium carbonate  $[\text{Ca}^{++}][\text{CO}_3'']$  is very small, and is consequently largely exceeded so that calcium carbonate is precipitated so long as calcium ions (from the slaked lime) and carbonate ions (from the sodium carbonate) are present in excess of the concentration corresponding to the solubility product of calcium carbonate. The concentration of calcium ions is, however, also determined by the solubility product of calcium hydroxide, i.e., by the product of the concentration of calcium ions and the square of the concentration of hydroxyl ions present. As the reaction proceeds the latter is increasing and hence the former (concentration of calcium ions) is decreasing. Consequently, a point will ultimately be reached when the concentration of calcium will have fallen to a value no longer in excess of that corresponding to the solubility product of calcium carbonate. At this point equilibrium will be established and the reaction will stop.

The fact that equilibrium is found to be more over to the calcium carbonate side of the equation the more dilute the solution is as a whole is what would be expected since the concentration of carbonate ion appears in the equations as the first power, whereas that of the hydroxyl ion is squared.

It is clear that from the manufacturers' point of view a compromise must be effected between the use of dilute solutions which give a purer product but which require a large expenditure for evaporation of the resulting caustic soda solution; and the use of concentrated solutions



which give products contaminated with carbonate but which are less costly to evaporate. In practice, the sodium carbonate solution used has a concentration of about 10 per cent and about 92 per cent causticization is effected.

### Manufacture of Caustic Soda by Electrolysis

Large and increasing quantities of caustic soda are now made by the electrolysis of solutions of common salt. Hydrogen and chlorine are formed at the same time. The process has been described in Chapter 25 (page 532).

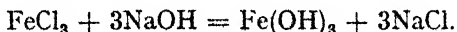
The caustic soda is obtained from these operations in the form of a strong solution from which the solid is obtained by methods similar to those described above.

The relative proportions in which caustic soda is manufactured by electrolysis and by the action of slaked lime on sodium carbonate solution is determined by the relative demand for chlorine and caustic soda. (Compare p. 533.)

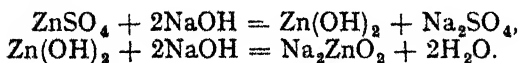
### § 14 Properties of Sodium Hydroxide

Sodium hydroxide is a white, crystalline solid which rapidly absorbs moisture and carbon dioxide from the atmosphere. It melts easily (at  $318.4^{\circ}$ ) and is sold in sticks, pellets or flakes formed from the molten material. It is very soluble indeed in water, and much heat is evolved during its solution. The solution has the characteristic soapy feel of an alkali, and is very corrosive. Sodium hydroxide is a very strong alkali; since, according to the Ionic Theory, it is very largely ionized in solution. It is only sparingly soluble in alcohol, in which it differs from potassium hydroxide (q.v.) which is very soluble.

Sodium hydroxide has the properties characteristic of a strong alkali. It changes the colours of indicators (e.g., litmus to blue, methyl orange to yellow; phenolphthalein to pink) and forms salts with all acids. It reacts with solutions of metallic salts (except salts of the alkali metals), precipitating the hydroxide of the metal, e.g., with ferric chloride:



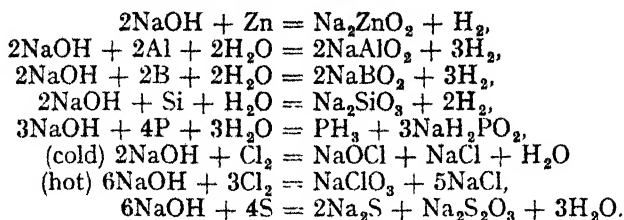
In some cases the metal hydroxide redissolves in excess of caustic soda solution, e.g., zinc:



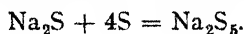
With ammonium salts ammonia gas is liberated, presumably on account of the very unstable nature of ammonium hydroxide (cf. Chapter 23, page 434).

Sodium hydroxide reacts with many free elements, both metals and non-metals. These reactions are considered in greater detail in the

chapters dealing with the elements concerned, but the reactions indicated by the following equations may be mentioned here:



This is probably the primary reaction, but the final product is the polysulphide formed by the action of excess of sulphur:



The above reactions take place in aqueous solution; fused sodium hydroxide will attack most metals (nickel and silver are only slightly attacked), and it also reacts readily with glass and porcelain, in fact, even the aqueous solution has an appreciable action on these materials.

### § 15 Uses of Sodium Hydroxide

Large quantities of sodium hydroxide, usually referred to commercially as caustic soda, are used in bleaching and dyeing, in the refining of oils and in the manufacture of soap and of paper. The largest single use is now in rayon manufacture which accounts for more than a quarter of the total production in Great Britain. The chemical industry in general uses about a quarter and a third quarter is shared between soap and papermaking. It is also used for the purification of bauxite (page 743) for the manufacture of aluminium; and in the production of dyes (e.g., alizarin). Sodium hydroxide, in the form of soda-lime (an intimate mixture of sodium hydroxide and slaked lime) is now often preferred to potassium hydroxide solution for the absorption of carbon dioxide in quantitative analysis. Specially prepared soda-lime for this purpose is sold under the names *sofnolite* and *ascarite*.

### § 16 Sodium Salts, Sodium Carbonate

Sodium hydroxide, being a very strong base, readily forms salts even with very weak acids. Sodium salts are colourless unless derived from a coloured acid, and are almost all soluble in water, the pyroantimonate ( $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ ) and the complex sodium magnesium uranyl acetate— $\text{NaMg}_2(\text{UO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_3$ —and the corresponding zinc triple acetate being the only important insoluble ones. Sodium salts often crystallize with considerable quantities of water.

### Sodium Carbonate, $\text{Na}_2\text{CO}_3$

Sodium carbonate has been known and used from the earliest times. Formerly it was made from the ashes of maritime plants (potassium carbonate was similarly obtained from the ashes of land plants), but at the end of the eighteenth century, largely through the stress of war conditions, alternative sources of supply became essential and a process of manufacture was devised by Leblanc which held its own for over a hundred years.

Sodium carbonate can be manufactured in four ways, viz.:

- (i) by the Leblanc process—now obsolete except as mentioned below;
- (ii) by the ammonia-soda (or Solvay) process;
- (iii) from naturally occurring sodium carbonate;
- (iv) from electrolytic caustic soda.

### The Leblanc Process

This process is now obsolete and has not been worked in this country since 1919 except (as mentioned on pages 538, 629) for the manufacture of sodium sulphate (salt-cake). It experienced a temporary revival in Germany after the 1914–18 war in a modified form for production of sodium carbonate from the large amounts of sodium sulphate accumulated at Stassfurt during that war, as a by-product from the extraction of potassium compounds. Similar use is being made of Russian deposits of natural sodium sulphate.

The Leblanc process proper was conducted in three stages:

- (i) The conversion of sodium chloride into sodium sulphate (called *salt-cake*) by heating it with sulphuric acid, as described on page 629:

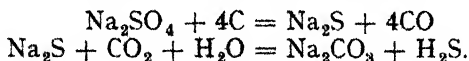


- (ii) The conversion of the salt-cake into *black ash* by heating to a high temperature in a revolving furnace with limestone and coke. Black ash is a mixture of calcium sulphide and sodium carbonate:



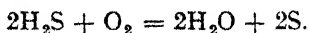
- (iii) The extraction of sodium carbonate from the black ash by leaching it with water, and purifying the product by crystallization. The calcium sulphide which remained (being insoluble in water) was used for the manufacture of sodium thiosulphate (see page 632).

In working the Stassfurt sodium sulphate into carbonate, use was made of reactions which dispense with the use of calcium carbonate, and sodium sulphide, made by reduction of the sulphate, page 629, was acted upon by a mixture of carbon dioxide and steam:



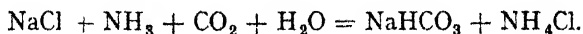
The sulphur can be recovered from the hydrogen sulphide by burning

the gas with the theoretical quantity of air in presence of iron oxide which acts as a catalyst



### The Ammonia-Soda, or Solvay, Process

This process depends upon the comparatively low solubility of sodium bicarbonate, particularly in presence of excess of carbon dioxide. When a concentrated solution of sodium chloride is saturated with ammonia and then with carbon dioxide, sodium bicarbonate is precipitated.

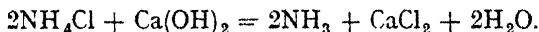


There have been several suggestions about the mechanism of this reaction; in the light of the evidence available it is sufficient to point out that of the possible combinations of the ions present in the solution (which are  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$ ) sodium bicarbonate is the one with the lowest solubility and so is precipitated.

The sodium bicarbonate formed is filtered off and heated, forming normal carbonate, carbon dioxide (which is used again) and steam.



The ammonia is recovered by heating the ammonium chloride solution with slaked lime.



The actual manufacture is carried out as follows:

The raw materials are *brine* (sodium chloride solution), usually obtained by direct pumping *in situ*; and *carbon dioxide*, obtained by heating limestone in kilns. The quicklime, produced at the same time, is used for the recovery of the ammonia. *Ammonia* is obtained in the first instance, or to make up loss in the process, similarly from external supplies of ammonia liquor, either synthetic or from gasworks.

Ammonia gas is forced up a tower down which strong brine (about 30 per cent  $\text{NaCl}$ ) is flowing. This is constructed as shown in Fig. 28.2. Heat is evolved in this process and so the ammoniated brine is cooled by passing over pipes through which cold water circulates.

The ammoniated brine is then made to run down a *carbonating tower* up which a stream of carbon dioxide is forced. The construction of this tower is indicated by Fig. 28.3. It consists of a series of sections, each about 6 ft. in diameter, and the whole tower is about 80 ft. high. The lower part of the tower is completely filled with ammoniated brine introduced through a pipe as shown. Carbon dioxide is forced in at the base and passes from section to section through perforated hoods: this ensures that the gas is well distributed through the liquid in small bubbles. Ammonia chloride and sodium bicarbonate are formed as indicated above; the latter, being precipitated, is carried out of the

base of the tower as a fine suspension. It is filtered off and washed to free it from ammonia and ammonium salts.

The sodium bicarbonate is then converted into the normal carbonate by heating in rotary calciners. The carbon dioxide evolved is returned to the plant, along with fresh supplies, and anhydrous sodium carbonate remains. This is known as **soda-ash**.

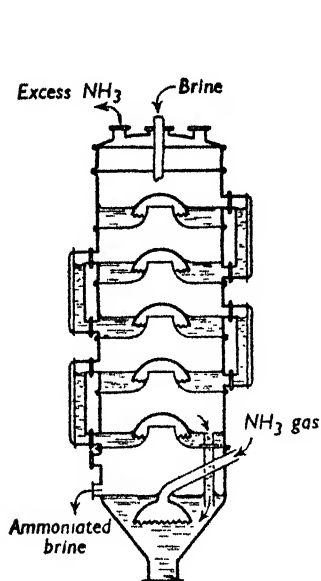


FIG. 28.2.—Ammonia Absorption Tower

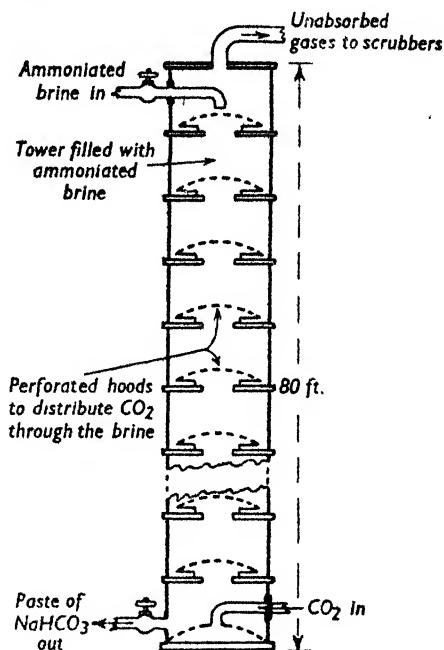


FIG. 28.3.  
Carbonating Tower

(Both from Durrant, *General and Inorganic Chemistry*)

From this soda-ash, various products are made. By dissolving it in water and crystallizing the solution, **washing-soda**,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , is obtained; while by evaporation  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , sold as **Mono**, is formed and crystallizes from the hot solution. The material sold under the name of **Sesqui**,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , results from crystallizing solutions containing equimolecular quantities of carbonate and bicarbonate.

This outline of the process indicates that limestone and salt along with water are the only raw materials (except fuel), and calcium chloride and waste mud (from the ammonia recovery section) the only waste products. The requirements in water, for the process, for cooling and for stripping ammonia and carbon dioxide from the filter liquor and ammonia for recovery after addition of slaked lime are very large.

Calcium chloride is a useful chemical but the demand for it is very small in comparison with the quantities produced. The mud arises from the silica and earthy impurities in the limestone used and is often left in the form of an intractable mixture which never settles from the calcium chloride liquor and is a jelly-like thixotropic substance which never dries out.

Fig. 28.4 illustrates diagrammatically the whole process.

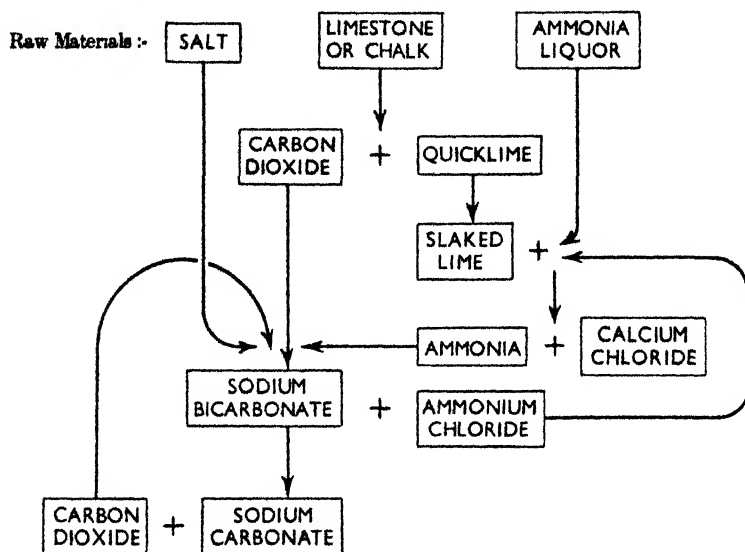


FIG. 28.4 —Solvay Process (diagrammatic)

### Sodium Carbonate from Natural Sources

There exist in certain areas (notably at Magadi in British East Africa, and in California) large deposits of sodium carbonate. These are now being utilized, particularly the Magadi deposits. They consist principally of the so called sesquicarbonate, commonly known as *trona*,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ . The "brine" of the lakes round whose shores these deposits are found is also treated for recovery of sodium carbonate.

### Sodium Carbonate from Electrolytic Caustic Soda

A considerable quantity of sodium carbonate is now being made from electrolytic caustic soda, particularly in America, where electrical energy is relatively cheap. Sodium chloride solution is electrolysed in a cell of the diaphragm type, thus producing caustic soda, hydrogen and chlorine. Crude carbon dioxide, from furnace gases, gas or oil-engine exhausts and similar sources, is blown through the liquid, thus

producing sodium carbonate which is recovered from the solution, as in other methods, by crystallization.

### Properties of Sodium Carbonate

Sodium carbonate can be obtained anhydrous, and also in combination with one, seven or ten molecules of water of crystallization. The anhydrous salt is a white solid which melts at  $851^{\circ}$  with slight decomposition.

As produced sodium carbonate is in the form known industrially as *light soda-ash* because the clusters of sodium bicarbonate crystals, when calcined, give rise to sodium carbonate in the form of a fine and dusty powder of bicarbonate pseudomorphs. For many industries this is acceptable but for export and for industries using the carbonate in furnaces dense grades are made by mixing the anhydrous carbonate with water to give the monohydrate which is then calcined. When crystallized from water, at a temperature below  $32^{\circ}$ , large transparent crystals of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  (washing-soda) are formed. These crystals effloresce (see page 247) when exposed to the air and gradually crumble to a white powder, probably  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . If exposed to the air for long periods, a little sodium bicarbonate is said to be formed. Crystallization of solutions between  $32^{\circ}$  and  $35.3^{\circ}$  causes deposition of the heptahydrate. Crystallization from solution between  $35.4^{\circ}$  and  $100^{\circ}$  yields the monohydrate. Other hydrates have been described, but their individuality is less well established.

Sodium carbonate is alkaline in solution owing to hydrolysis (see page 268) and is frequently used in volumetric analysis as a standard alkali. It is readily decomposed by acids (cf. page 341) with evolution of carbon dioxide.

Sodium carbonate is used for softening water, and the alkalinity of the resulting solution enhances the detergent properties of the water. Large quantities are used in the manufacture of caustic soda (page 615), of glass, probably the largest single use (page 778), of water glass (sodium silicate, page 771), of paper, and of borax (page 739). It is also a constituent of many patent soap powders, and is the starting point for the preparation of a number of other sodium salts. Soda-ash is also now being used in the smelting of certain iron ores of high sulphur content (Brassert process), the manufacture of dyestuffs and tar and oil distillation.

**Sodium bicarbonate, Sodium hydrogen carbonate,  $\text{NaHCO}_3$ ,** is produced in large quantities as the primary product of the ammonia-soda process; but is converted into the normal carbonate as described above. Commercial sodium bicarbonate is made by distilling a magma of crude bicarbonate with steam. This removes ammonia and carbon dioxide and eventually the magma is decarbonated sufficiently to leave a clear solution. This clear solution is treated again with carbon dioxide to precipitate refined bicarbonate of soda.

Refined sodium bicarbonate, made in this way, is noteworthy for its

purity for, while being manufactured at the rate of some hundreds of tons per day, it is pure enough to comply with the stringent requirements of the British Pharmacopoeia. It is one of the purest industrial chemicals known.

Sodium bicarbonate forms small white crystals which are somewhat sparingly soluble in water. 100 grams of water will dissolve 6.9 grams at 0°. The solution is slightly alkaline owing to partial hydrolysis, since sodium hydroxide is a very strong base while carbonic acid is a very weak acid. Sodium bicarbonate decomposes at 100° with evolution of carbon dioxide and steam, the normal carbonate being left.

Sodium bicarbonate is used in baking powders (and hence is sometimes known as *baking-soda*); it is also an important constituent of health salts, and "Seidlitz powders." Other uses are for sheathing explosives for use in coal mines, in fire extinguishers, leather manufacture and for water conditioning in breweries.

**Sodium sesquicarbonate**,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ , known commercially as *sesqui*, is obtained in a similar, suitably modified process, to that used for the bicarbonate. It is extensively used in wool-washing, for bath salts, in some packeted detergents and for cream neutralization.

## § 17 Sodium Halides

### Sodium Chloride, NaCl

Sodium chloride, usually known as *common salt* or simply *salt*, is not only the most important source of sodium compounds, but is also important for itself. Its occurrence has been referred to already (page 610). The production of salt from these natural sources is an important operation.

### Manufacture of Common Salt

According to the circumstances, salt is either mined, or extracted from salt beds by solution in water (i.e., in the form of *brine*) or got from the sea by evaporation.

Salt is mined in many parts of the world and the solid salt is crushed and sieved. As so obtained, it is usually impure and, though used in this state for some purposes, it is mostly purified by being dissolved in water and crystallized as described below.

In many salt beds (e.g., in Cheshire) the salt is obtained by forcing water into the beds through a boring or well. The brine so formed is afterwards pumped to the surface and the liquid concentrated, usually in multiple effect evaporators under reduced pressure, but sometimes also in large shallow open pans heated by coal fires.

The multiple effect evaporators (Fig. 28.5) consist of a series of closed vessels, so arranged that the steam resulting from the evaporation in one heats the next, in which the pressure is lower. The first of the series is heated with live steam from a boiler, and the last is connected to an exhaust pump. Brine is fed continuously to the evaporators and the



salt formed is withdrawn as a slurry in brine. The salt is separated from the slurry by filtration or in a centrifuge and the filtrate is returned to the evaporators.

The greater part of the salt produced by vacuum evaporation is in the form of fine-grained cubic crystals but, by modification of the process, coarse-grained and flaky crystals of salt can be made for use in circumstances where these characteristics are of value.

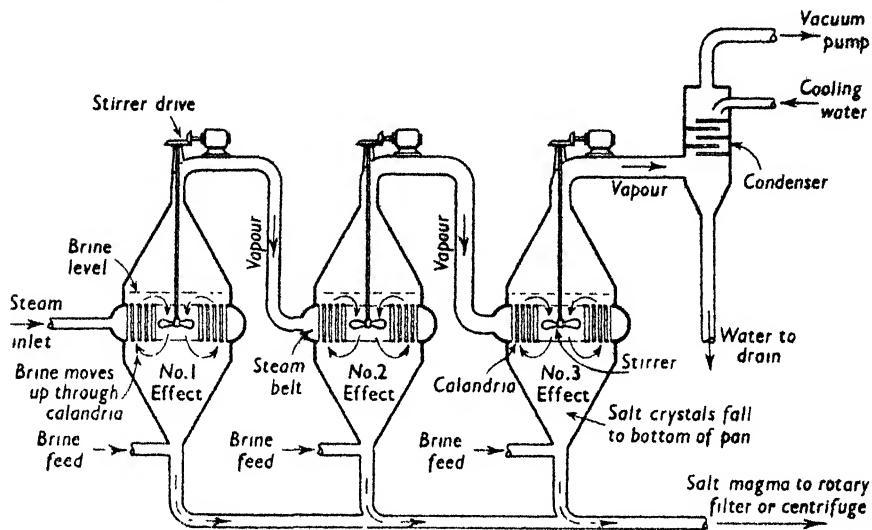


FIG. 28.5 —Multiple Evaporation

Some salt is still produced by the old process in which brine is kept slightly below its boiling point in large shallow pans. Crystallization takes place mainly on the surface of the brine and the salt produced has a flaky crystalline form. The size and character of the crystals can be controlled by varying the temperature of the brine and the length of time for which crystals are allowed to grow.

The production of salt from sea-water is only practicable in warm countries or where fuel is very cheap. It is carried on, for instance, in the *salterns* or salt gardens on the shores of the Mediterranean Sea, where the sea-water is concentrated by evaporation in large shallow tanks—"salterns"—exposed to wind and sun. As the solution—"brine"—becomes concentrated, the crystals of salt—*bay salt*—which separate are lifted out by means of perforated shovels, and allowed to drain beside the evaporation tanks. The crystals are allowed to stand in heaps exposed to occasional showers, whereby much of the magnesium chloride is leached out. The product is sometimes called *solar salt*. The mother liquid—"bittern"—was once used for the manufacture of bromine,

The salt obtained by these methods is contaminated with small quantities of other salts as impurities: calcium chloride, magnesium chloride, calcium sulphate, and magnesium sulphate.

Salt produced by vacuum evaporation may contain over 99.9 per cent of sodium chloride. Salt produced by the open pan process, or by solar evaporation, usually contains about 97 to 99 per cent of sodium chloride; the sodium chloride content of rock salt usually lies between 95 and 99 per cent.

### The Purification of Sodium Chloride

Sodium chloride can be purified by adding concentrated hydrochloric acid to a cold saturated aqueous solution of salt; better results are obtained by passing gaseous hydrogen chloride through the salt solution. The impurities remain in solution while the sodium chloride is precipitated in a very fair state of purity.

This effect is explained by the Ionic Theory as a consequence of the common ion effect (page 263). The addition of the very soluble hydrogen chloride gas increases largely the concentration of chloride ion, thus causing the solubility product of the salt (the solution being already saturated) to be largely exceeded, salt being precipitated in consequence.

### Properties of Sodium Chloride

Sodium chloride crystallizes in cubes and the crystals are anhydrous though a little water may be mechanically entangled in them. The melting point is  $804^{\circ}$  and it boils at  $1413^{\circ}$ . Sodium chloride is quite soluble in water, 100 grams of water dissolving 36 grams of salt at  $20^{\circ}$ . The solubility is only very slightly affected by temperature (cf. Fig. 13.2, page 130). Thus 100 grams of water will dissolve 35.7 grams of salt at  $0^{\circ}$  and 39.8 grams at  $100^{\circ}$ . Sodium chloride is almost insoluble in alcohol.

### Uses of Sodium Chloride

In addition to its use for seasoning food (for which purpose it should preferably be freed from magnesium and calcium chlorides), common salt is also used for preserving butter, meat and fish, etc., as a starting point for the manufacture of caustic soda (page 615), sodium carbonate (page 620) and of sodium metal and sodium compounds in general. It is also used in the course of soap manufacture for "salting-out" the soap; in glazing common pottery (e.g., drainpipes, etc.) and for the manufacture of chlorine and hydrochloric acid (pages 532, 538) and hence of chlorine compounds in general. It is also employed in large quantities for melting snow and ice on roads and for the regeneration of base-exchange water-softening plant (p. 311).

**Sodium fluoride**, NaF, forms colourless crystals resembling the chloride. It can be made by neutralizing hydrofluoric acid with sodium hydroxide or sodium carbonate. It can also be prepared from cryolite

( $\text{AlF}_3 \cdot 3\text{NaF}$ ) by treatment with excess of sodium hydroxide solution. This dissolves the aluminium fluoride, and the undissolved sodium fluoride is extracted with boiling water. It has been used as a mild disinfectant.

**Sodium bromide**,  $\text{NaBr}$ , and **sodium iodide**,  $\text{NaI}$ , are not much used, the potassium salts being preferred. They are made in the same way as the potassium salts (q.v.). Both bromide and iodide crystallize with two molecules of water of crystallization.

### Sodium Nitrate, Chile Saltpetre, $\text{NaNO}_3$

Large quantities of sodium nitrate occur in Argentina, California, and principally in the rainless districts of the west coast of South America—Peru, Bolivia and Chile. Here the salt occurs in large flat basins, illustrated diagrammatically by Fig. 28.6.



FIG 28.6 - Geological Section of Nitre Bed (diagrammatic)

There is a thin surface layer of sand and pebbles, below which is a 1- to 5-foot layer of similar material bound together with clay, salt and sodium nitrate. This layer is known as *costra* and contains 5 to 12 per cent of nitrate. Below this is a white stratum of similar thickness, known as *caliche*, which contains an average of 20 to 30 per cent of sodium nitrate. Below the caliche is a layer of salt, etc., resembling *costra*, a layer of clay, and finally the bed rock of shale and limestone.

The problem of the origin of these nitre beds has not been satisfactorily solved, although it is generally agreed that the nitrogen is of organic origin. Possibly they are derived from guano, immense deposits of which exist on the islands off the coast of Peru (though the absence of phosphate in the nitre beds would then have to be explained); possibly they are derived from masses of seaweed which have decayed.

The caliche is mined by boring down to the lowest stratum. The bore is enlarged and charged with blasting powder. The explosion breaks up the nitre bed within a 50-foot radius of the explosion. The caliche is sorted out and transported to the leaching works. The caliche is extracted with water, and the solution is recrystallized so as to separate the sodium nitrate from the accompanying impurities—sodium chloride, sodium and calcium sulphates, sodium iodate, sodium perchlorate, insoluble matter, etc. Commercial Chile salt-petre contains from 95 to 98 per cent of sodium nitrate. The sodium iodate which accumulates in the mother liquor is used for the manufacture of iodine (q.v.).

Sodium nitrate forms white, cubic crystals. It is very soluble in

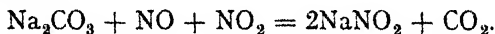
water: 100 grams of water at 20° dissolve 88 grams of the salt. It melts at 308°, and decomposes at a higher temperature into oxygen and sodium nitrite. Large quantities are used for fertilizers; it is also important for the manufacture of nitric acid, potassium nitrate, sodium arsenate, sodium nitrite, glass, and fireworks, and for curing meat, etc.

The output of natural sodium nitrate from Chile has declined somewhat of late owing to the development of processes for the fixation of nitrogen (see Chapter 23), and a certain amount of sodium nitrate is now made from synthetic nitrogen compounds. In one method, nitrogen oxides (from ammonia-oxidation) are absorbed in caustic soda solution, and the resulting liquor mixed with nitric acid and blown in a tower with enriched air (50 per cent or more oxygen). Attempts are also being made to produce sodium nitrate from nitric acid and sodium chloride; from oxides of nitrogen and sodium chloride; and from sodium sulphate and nitric acid.

### Sodium Nitrite, $\text{NaNO}_2$

Sodium nitrite is of technical importance in the dyestuffs industry, and is now made on a considerable scale. It is formed by heating sodium nitrate alone above its melting point, and it used to be made by reducing the nitrate with lead or a mixture of carbon and lime, which enables the conversion to be effected at a lower temperature.

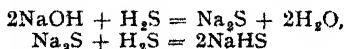
It is now manufactured almost entirely in the course of the processes for the fixation of atmospheric nitrogen (pages 448-9), being produced by absorbing the final gases from the ammonia oxidation in sodium carbonate solution:



Sodium nitrite is a white, crystalline compound when pure, but is usually slightly yellow as obtained. It has a high solubility in water: 100 grams of water will dissolve 77.6 grams of the salt at 15°, and much heat is absorbed during solution.

### Sodium Hydrosulphide, $\text{NaHS}$

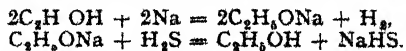
Sodium hydrosulphide is formed in solution when aqueous sodium hydroxide is saturated with hydrogen sulphide, but, on account of hydrolysis, the anhydrous salt cannot be obtained from this solution, the hydrate  $\text{NaHS} \cdot 3\text{H}_2\text{O}$  results:



It can be obtained anhydrous by heating sodium with hydrogen sulphide gas:



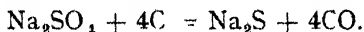
(compare action of sodium on water), or by the action of hydrogen sulphide on sodium ethoxide (the product of the action of sodium on alcohol):



Sodium hydrosulphide is a white, deliquescent solid which forms the normal sulphide on heating.



**Sodium sulphide**,  $\text{Na}_2\text{S}$ , is formed when the correct amount of hydrogen sulphide is passed into excess of caustic soda solution, or by heating the hydrosulphide, or by adding caustic soda solution in correct amount to the solution of the hydrosulphide. It is now manufactured on a considerable scale, from sodium sulphate. Sodium sulphate is reduced by heating it with coal at  $1000^\circ$  in a revolving furnace, carbon monoxide being formed at the same time:



The mass, *black ash*, is extracted with water and the solution evaporated to give crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ . The mother liquor is used for the production of sodium thiosulphate (below).

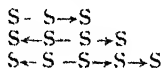
Sodium sulphide is a buff-coloured solid. It is used extensively in the production of dyes. It is used also for removing the hair from hides before tanning.

#### Sodium Polysulphides, $\text{Na}_2\text{S}_n$ - ( $n = 2$ to 5)

Free sulphur is fairly soluble in solutions of soluble sulphides, such as those of the alkali metals, and the resulting solutions contain various polysulphides. Thus, from sodium sulphide is formed a series ranging from the monosulphide itself to the pentasulphide  $\text{Na}_2\text{S}_5$ . Polysulphides are also formed by direct union of sulphur and sodium. The exact composition and relation between these substances have not been clearly demonstrated, and it is probable that most samples are mixtures of various polysulphides. They are yellow in colour, on exposure to the air they are oxidized to thiosulphates and sulphur



With acids, hydrogen persulphide (page 486) or hydrogen sulphide, and sulphur are formed according to the conditions. The constitution of the bivalent polysulphide ions probably involves co-ordinate links, thus



### § 18 Sodium Sulphates and Sulphites, etc.

#### Sodium Sulphate, $\text{Na}_2\text{SO}_4$

Sodium sulphate is an important industrial chemical for which there is an increasing demand. Formerly very considerable quantities were made from nitre-cake (crude sodium bisulphate), which was a by-product of the manufacture of nitric acid (page 447). Supplies of nitre-cake are now diminishing, through the increased production of synthetic nitrates, and the main supply of sodium sulphate is now derived from

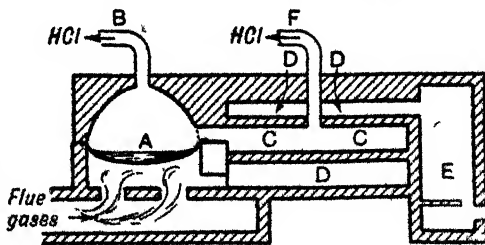
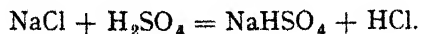
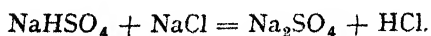


FIG 28 7.—Salt Cake Furnace

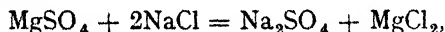
the action of concentrated sulphuric acid upon common salt, as in the first stage of the now obsolete Leblanc process (cf. page 619). Two molecular proportions of salt and one of concentrated sulphuric acid are heated by means of flue gases in a shallow cast-iron pan *A* in a furnace arranged as in Fig. 28.7. The temperature is such that sodium hydrogen sulphate is formed and hydrogen chloride escapes through the flue *B*.



When this reaction is complete the mass, which is now pasty, is raked into the closed muffle *C* which is heated externally to redness by means of producer gas burning around it in *D*. *E* is the producer. Sodium sulphate is then formed and more hydrogen chloride is evolved and led off through *F*.



Considerable quantities of sodium sulphate are also obtained as a result of the working of the Stassfurt deposits. The residues from the manufacture of potassium chloride from carnallite (page 640) contain a large amount of magnesium sulphate. These residues are dissolved in water and treated with common salt. From the solution  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  separates, being the least soluble of any of the four salts in the equation:



provided that the conditions (e.g., concentration) are so adjusted that *astrakanite*— $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ —is not formed.

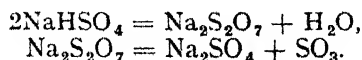
Sodium sulphate occurs native in many parts, particularly in the Western States of America, the western provinces of Canada, and in Russia, and these are now being worked extensively.

Anhydrous sodium sulphate is a white solid which is fairly readily soluble in water. Solutions which crystallize below  $32^\circ$  deposit the decahydrate  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  known as *Glauber's salt*. A heptahydrate is also known, and is formed by cooling supersaturated solutions of the salt to  $5^\circ$ . Sodium sulphate is one of the easiest salts with which to demonstrate the phenomenon of supersaturation.

Sodium sulphate is used in large quantities in the manufacture of glass (page 778) and of kraft paper. It was formerly made for conversion into sodium carbonate in the Leblanc process; it is still used for making sodium sulphide and sodium thiosulphate (q.v.) and is sometimes employed, instead of the carbonate, for making water-glass (page 771). A recent use, which is assuming large proportions, is as a constituent of synthetic detergents. It is used in the dyeing and textile industry and Glauber's salt is employed medicinally. Considerable quantities are converted into sodium bisulphate for use in the working of copper-nickel ores.

**Sodium Hydrogen Sulphate, Sodium Bisulphate,  $\text{NaHSO}_4$** 

This salt is the product of the action of concentrated sulphuric acid on sodium chloride or nitrate at temperatures below red heat (pages 447, 538). The crude product of the nitric acid industry is known as *nitre-cake*. It can be prepared in the laboratory by mixing a solution of two equivalents of sulphuric acid with one equivalent of caustic soda, when  $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$  crystallizes from the solution in white crystals. This can be dehydrated by heat, and the anhydrous salt can be fused at  $300^\circ$ . At higher temperatures, it decomposes into **sodium pyrosulphate**,  $\text{Na}_2\text{S}_2\text{O}_7$ , which, on further heating, gives sodium sulphate and sulphur trioxide:



It is used in the form of nitre-cake in the manufacture of hydrochloric acid and sodium sulphate (pages 538, 629) and in the laboratory for breaking down some minerals prior to analysis. It is used as a fluxing agent in the extraction of copper-nickel ores and is a constituent of commercial products such as *harpic*.

**Sodium Sulphite,  $\text{Na}_2\text{SO}_3$** 

If a solution of caustic soda be divided into two equal parts and one is saturated with sulphur dioxide and then mixed with the other the mixture on evaporation deposits crystals of the composition  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ . On the large scale it is made by passing sulphur dioxide through a solution of sodium carbonate, or through a vessel filled with crystals of washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), until the mixture has an acid reaction. Steam is blown in to prevent deposition of crystals of the bisulphite, after which sodium carbonate is added to the boiling solution until no more carbon dioxide is evolved. The liquid is then evaporated to crystallizing point.

Sodium sulphite forms colourless crystals which are anhydrous if crystallized above  $22^\circ$ , and contain seven molecules of water if separated below that temperature. It is readily soluble in water: 100 grams of water dissolve 25 grams of anhydrous salt at  $15^\circ$ . The solution undergoes oxidation when exposed to the air, sodium sulphate being formed (cf. page 491).

Solutions of sodium sulphite are used as a gentle bleaching agent for wool or silk, as an "antichlor" (page 535) after bleaching with chlorine, as a preservative for foodstuffs, and in the refining of sugar. It is used in photography as a constituent of developers.

**Sodium Hydrogen Sulphite, Sodium Bisulphite,  $\text{NaHSO}_3$** 

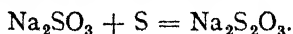
This is produced in solution by saturating a solution of sodium carbonate with sulphur dioxide. It can be isolated from this solution, by precipitation with alcohol, as a white powder. On heating it decomposes

into the sulphate, sulphur dioxide and sulphur. It is used as an anti-chlor, and as an antiseptic for preserving food and for sterilizing brewers' casks. It is also a useful reagent in organic chemistry.

### Sodium Thiosulphate, $\text{Na}_2\text{S}_2\text{O}_3$

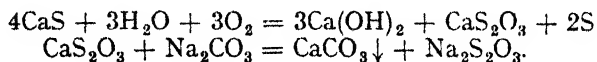
This salt was formerly (wrongly) termed sodium hyposulphite and is still so called by photographers. It has been discussed to some extent already (page 512) in connection with thiosulphates in general.

Sodium thiosulphate can be prepared in the laboratory by heating a solution of sodium sulphite with free sulphur:

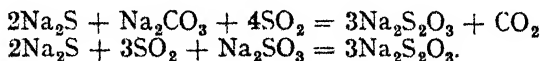


This reaction is formally analogous with the oxidation of sodium sulphite by atmospheric oxygen; hence the name *thiosulphate*. It is interesting to note that if a sample be made thus, using a radioactive isotope of sulphur, the radioactive thiosulphate, on acidification, deposits the whole of its radio-sulphur as a precipitate of free sulphur; the sulphur dioxide liberated being non-radioactive. This seems to suggest that the two sulphur atoms in a thiosulphate are not equivalent.

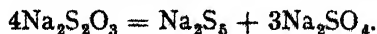
Sodium thiosulphate was formerly extensively manufactured from the alkali-waste (page 619) of the Leblanc process by exposing it to the air for some days, lixiviating with water, adding sodium carbonate, and evaporating and crystallizing the remaining solution. The actions taking place may be represented as in the equations below, but the oxidation is undoubtedly complex and there are probably several intermediate stages:



It is now made from the waste liquors obtained in the production of sodium sulphide. The crude liquor, obtained by dissolving the melt (page 629), contains, in addition to the sulphide, sulphate, carbonate and sulphite. On concentration, these salts are deposited and are filtered off, dissolved in water and treated with burner gases containing sulphur dioxide. Sodium thiosulphate is formed according to the equations:



Sodium thiosulphate forms large colourless crystals of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  when it separates from water. It is freely soluble in water. On heating, it decomposes into sodium sulphate and pentasulphide:



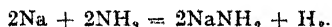
The action of acids has been mentioned on page 512 and of iodine solutions on page 567. The former reaction is used qualitatively for the detection of thiosulphates; the latter is of great importance in



quantitative volumetric analysis. Some of its applications are referred to on page 567.

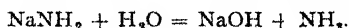
### § 19 Sodamide and Sodium Cyanide

**Sodamide**,  $\text{NaNH}_2$ , is prepared by the action of dry ammonia gas on metallic sodium heated to a temperature of  $300^\circ\text{--}400^\circ$  in an iron vessel. The reaction may be represented:



The hydrogen escapes along with the excess of ammonia.

Sodamide is a white wax-like solid, which is decomposed by water:

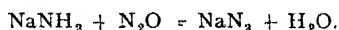


When heated in carbon dioxide, cyanamide is formed:



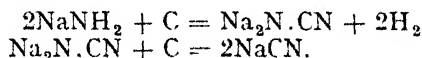
Sodamide is used as an intermediate product in the manufacture of sodium cyanide (see below), in the dyestuffs industry and as a condensing agent in organic chemistry.

When sodamide is heated in a stream of dry nitrous oxide, **sodium azide**,  $\text{NaN}_3$ , is formed. This is used as a reagent in organic chemistry and for the preparation of lead azide which is used as a detonator:

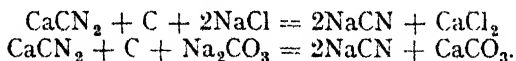


### Sodium Cyanide, $\text{NaCN}$

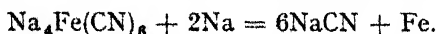
Sodium cyanide is now manufactured in large quantities, mostly from metallic sodium. Metallic sodium is converted into sodamide (as above) by the action of ammonia, and this is then run on to red-hot charcoal. Sodium cyanamide is first formed which then reacts with more carbon forming the cyanide:



Crude sodium cyanide (suitable for gold extraction) is also made by fusing calcium cyanamide (nitrolim—page 424) with salt or sodium carbonate:

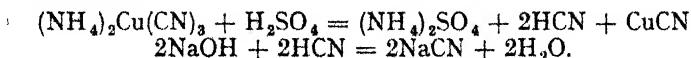


Sodium cyanide is also prepared on a considerable scale from the hydrocyanic acid extracted from crude coal gas. One method of doing this is to convert it into potassium (or sodium) ferrocyanide (page 382) which, when fused with sodium, yields sodium cyanide:

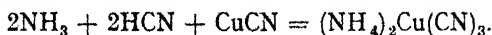


Another (and probably better) process consists in passing the crude gas (containing ammonia as well as hydrocyanic acid) through solutions of copper salts whereby ammonium cuprocyanide— $(\text{NH}_4)_2\text{Cu(CN)}_3$ —is formed. Dilute sulphuric acid is then added and the liberated

hydrocyanic acid is absorbed in caustic soda solution, thereby forming sodium cyanide:



The cuprous cyanide formed is insoluble and is used again for the absorption of HCN:



Sodium cyanide is a white crystalline substance and, like all cyanides, is extremely poisonous. It is soluble in water, and the solution, owing to hydrolysis (page 269), is strongly alkaline and smells of hydrocyanic acid.

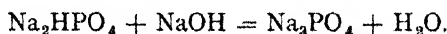
Sodium cyanide is used in large quantities for the extraction of gold and silver from their ores (pages 674, 664), and in the laboratory it is employed in the preparation of other cyanides, of some organic compounds and as a reducing agent. It is used industrially for case-hardening iron, in the electroplating industry, and is the raw material for the production of hydrocyanic acid for spraying fruit trees, fumigation, destruction of vermin, etc.

## § 20 Sodium Phosphates

### Sodium (ortho) Phosphates

(Ortho) Phosphoric acid is a tribasic acid and hence should form three sodium salts. These are all known.

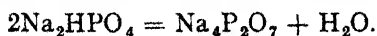
**Normal sodium phosphate**,  $\text{Na}_3\text{PO}_4$ , is usually made by adding the theoretical amount of sodium hydroxide solution to a solution of disodium hydrogen phosphate (the ordinary "sodium phosphate" of commerce and the laboratory):



On evaporation, white crystals of  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  separate. It is readily soluble in water and its solutions are strongly alkaline owing to hydrolysis. It is used commercially under the name *tripsa* for softening boiler feed water: the temporary hardness is removed by precipitation as carbonate owing to presence of free alkali, and permanent hardness is removed also since calcium and magnesium, if present as sulphate or chloride, are both precipitated as phosphates. It is also used as a detergent and degreasing agent; as an emulsifier in cheese-making and for photographic purposes.

**Disodium hydrogen phosphate**,  $\text{Na}_2\text{HPO}_4$ , is the ordinary "sodium phosphate" of the laboratory. It is made by "neutralizing" phosphoric acid with sodium carbonate or caustic soda, using phenolphthalein as indicator. It crystallizes with twelve molecules of water of crystallization, and is used as a reagent in the laboratory. It is

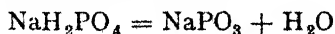
efflorescent, forming  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  in ordinary air. It is very soluble in water. On heating, it loses water, forming **sodium pyrophosphate**:



"Sodium phosphate" is used in the textile industry and for dye-making, and in large quantities in domestic packeted detergents.

**Sodium dihydrogen phosphate**,  $\text{NaH}_2\text{PO}_4$ , is made by adding phosphoric acid to a solution of the "ordinary" phosphate until a precipitate is no longer formed when a drop of the solution is added to barium chloride solution. Alternatively, the end point may be fixed by the use of methyl orange as indicator. On evaporation, it crystallizes out as  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ , in white crystals which are readily soluble. It is used as a constituent of some baking powders.

The action of heat on sodium dihydrogen phosphate is usually said to convert it into sodium metaphosphate,



but the exact nature of the product varies according to the conditions. If the heating be carried out between  $550^\circ$  and  $628^\circ$  (the melting point) the product is almost entirely sodium trimetaphosphate,  $\text{Na}_3\text{P}_3\text{O}_9$ . If the substance be fused, and then cooled rapidly, a glass results, known as *Graham's salt* and frequently described as **sodium hexametaphosphate** and given the formula  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$  but there is little or no experimental evidence in support of the name or formula; this compound is, in all probability, a highly polymerized sodium metaphosphate. Under the trade name *Calgon* it is used for softening water (page 312. Cf. also page 827 where metaphosphoric acid and the metaphosphates are dealt with in greater detail).

**Sodium ammonium hydrogen phosphate, microcosmic salt**,  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ , is formed by dissolving equimolecular amounts of ammonium chloride and ordinary sodium phosphate in a little hot water, filtering off the sodium chloride precipitated and crystallizing. It is used in qualitative analysis for "bead" tests.

## § 21 Detection and Determination of Sodium

Sodium compounds give an intense yellow colour to the bunsen flame; but as a test this needs to be used with caution, as it is so extremely sensitive that a minute trace of sodium as impurity might be interpreted wrongly.

Sodium may be detected (in a solution from which all metals but the alkali metals have been removed) by addition of a solution of potassium pyroantimonate (page 848), and allowing the mixture to stand, when a white crystalline precipitate of sodium pyroantimonate ( $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7$ ) indicates the presence of sodium. Sodium is also precipitated in similar circumstances from solutions containing zinc and uranyl acetates as

yellow sodium zinc uranyl acetate— $\text{Na}_2\text{Zn}(\text{UO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_2$ . The corresponding magnesium compound can also be used in this way.

Sodium is usually determined as sulphate. Other metals are removed first (as above) and the remaining solution evaporated with sulphuric acid in a platinum basin or crucible until no further loss of weight occurs. The use of triple uranyl acetates mentioned above for the quantitative determination of sodium is being developed.

## § 22 Potassium, K

### History and Occurrence

Potash—the potassium carbonate obtained from the ashes left after wood and land plants have been burned—has long been known; but it was confused with soda, from which it has been clearly distinguished only since the eighteenth century. Metallic potassium was first obtained by Sir H. Davy in 1807 by the electrolysis of fused potassium hydroxide.

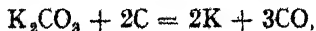
Potassium probably occurs in the earth's crust, to an extent about equal to that of sodium, but its compounds are much less easily accessible; the occurrence of large deposits of sodium chloride in most parts of the world providing a ready and almost unlimited source of sodium compounds. By comparison, workable deposits of potassium compounds are relatively scarce. At one time the principal source of the world's supplies of potassium compounds was the Stassfurt deposits (page 529), but during the war of 1914–18 other sources of supply were brought into use. Thus a certain amount of potassium salts was obtained from orthoclase, a felspar consisting of potassium aluminosilicate, and also as a by-product of blast-furnace operation. More recently workable deposits of potassium compounds have been discovered, particularly in the Dead Sea, Canada, the U.S.A. and in Russia.

All land plants contain considerable quantities of potassium compounds, which are derived from the soil. Under cultivation this is lost from the soil and must be replaced if its fertility is not to be impaired. Hence suitable potassium compounds are important as fertilizers.

It is noteworthy that, notwithstanding the fact that potassium compounds are usually at least as soluble as the corresponding sodium salts, the proportion of the former in the sea is very small. This has been attributed to the adsorptive power of the soil for potassium ions being much greater than for sodium ions.

### Preparation of Potassium

Potassium has been made by heating potassium carbonate with charcoal:



but explosions are liable to occur when it is made in this way, owing to the formation of potassium carbonyl,  $\text{K}_2(\text{CO})_2$ . Potassium can be obtained in the same way as sodium, by electrolysis of the fused

hydroxide, but the process is not altogether satisfactory owing to the greater readiness with which the liberated metal dissolves in the fused alkali. It is more satisfactorily obtained using the fused cyanide. It can also be made by heating potassium hydroxide or sulphide with magnesium, aluminium or iron; or by heating potassium fluoride and calcium carbide. But it is not made on any great scale, as sodium will serve equally well for almost all purposes. It is used to some extent (like sodium) for photo-electric cells (cf. page 613), and it is occasionally required in the laboratory, particularly in organic chemistry.

### Properties

Potassium is a silvery white metal, which rapidly tarnishes when exposed to the air. It is less dense than water (density 0.86 at 20°). It melts at 63° and boils at 760°.

The chemical properties of potassium very closely resemble those of sodium, but its reactions are more vigorous. Thus, when dropped on water the hydrogen evolved, even from a very small piece of potassium, bursts into flame.

Potassium is noteworthy in being very feebly radioactive, emitting  $\beta$ -rays (cf. page 137). Potassium exists in three isotopes of mass numbers 39, 40 and 41 respectively; the radioactivity is due to the isotope of mass number 40, present to the extent of 0.012 per cent.

### Atomic Weight

The atomic weight of potassium has been found in a similar manner to that of sodium; and also by converting a weighed quantity of pure potassium chlorate into chloride by heat.

The value at present recommended by the International Committee is 39.10.

## § 23 Hydride and Oxides of Potassium

### Potassium Hydride, KH

Potassium combines with hydrogen in the same way as sodium, forming slender white needles of the hydride. It is decomposed by water or by heat with formation of hydrogen. Like sodium hydride it combines with carbon dioxide with the formation of the corresponding formate.

### Oxides of Potassium

Potassium forms two well-characterized oxides, viz.:

Potassium monoxide,  $K_2O$ ,  
Potassium dioxide,  $KO_2$ .

Others have been reported, but their existence is doubtful.

**Potassium monoxide,  $K_2O$ ,** is obtained by oxidation of potassium in air or oxygen under reduced pressure, any unoxidized potassium remaining being removed by distillation *in vacuo*. It closely resembles sodium monoxide in behaviour.

**Potassium Dioxide,  $\text{KO}_2$** 

This oxide is formed as a chrome-yellow powder by burning potassium in air or oxygen, moisture being rigorously excluded. It acts upon water, forming hydrogen peroxide and oxygen, if the temperature be kept down:



If the temperature rises, the hydrogen peroxide is decomposed.

Potassium dioxide, when heated with carbon monoxide, yields potassium carbonate and oxygen:



This oxide was formerly thought to have the formula  $\text{K}_2\text{O}_4$ , but X-ray and magnetic measurements support the simpler formula  $\text{KO}_2$ .

**§ 24 Potassium Hydroxide,  $\text{KOH}$** 

Potassium hydroxide is made in a similar manner to sodium hydroxide (q.v.). Electrolysis of solutions of potassium chloride is the method now most commonly used; but it has also been made by the action of lime on solutions of the carbonate or sulphate.

It closely resembles sodium hydroxide in properties, but is more soluble both in water and particularly in alcohol. It melts at  $360^\circ$ . Its solution in this latter solvent is an important reagent in organic chemistry. Potassium hydroxide (or caustic potash) is a very hygroscopic substance and is used as a drying agent for gases; it is also employed for the absorption of gases such as carbon dioxide or sulphur dioxide. It is preferred for this latter purpose over sodium hydroxide owing to the much smaller tendency of the carbonate or sulphite to crystallize out of solution, blocking the flow of gas. Another important industrial use is for the electrolyte in the nickel-iron storage battery.

It is used for the manufacture of soft soap. (Caustic soda yields hard soap.)

**§ 25 Potassium Salts**

Potassium salts very closely resemble the corresponding sodium salts. They do not exhibit the same tendency to separate from solution with water of crystallization, and they are often less hygroscopic and hence are preferred for certain purposes. Thus, potassium nitrate in gunpowder, and the potassium salts of acids such as hydriodic, chloric, chromic, permanganic and hydroferrocyanic, being easier to keep on this account, are more commonly used than the sodium salts.

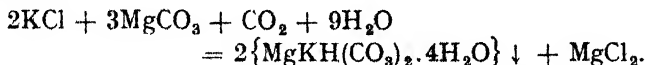
**Potassium Carbonate,  $\text{K}_2\text{CO}_3$** 

Under the name potash, or pot-ashes, this salt has been known since very early times.

It can be made from potassium chloride by the Leblanc process,

exactly as described above for sodium carbonate, except that it will not crystallize out from the liquor obtained after lixiviation of the black ash, and is obtained by evaporating to dryness.

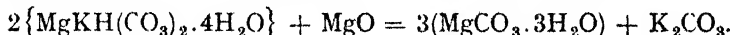
The Solvay process cannot be used for the production of potassium carbonate on account of the too great solubility of the bicarbonate. It is usually made, however, by **Precht's process** in which solid hydrated magnesium carbonate is added to a concentrated solution of potassium chloride. Carbon dioxide is passed in and a precipitate of magnesium potassium hydrogen carbonate— $\text{MgKH}(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$ —is formed, which is filtered off:



This precipitate is either treated with water at  $140^\circ$  under pressure when insoluble magnesium carbonate and potassium carbonate solution are formed:



or with a suspension of magnesium oxide in water below  $20^\circ$ :



In either case the magnesium carbonate is filtered off and used again. Potassium carbonate is also made by the action of carbon dioxide on potassium hydroxide solution.

Potassium carbonate is extracted from various animal and vegetable products. Thus the *suint* (the oily sweat) extracted from raw wool (which contains up to 30 per cent of suint) contains a considerable quantity of potassium carbonate which is recovered by evaporation of the liquors used for washing the raw wool. A certain amount is also recovered from the residues from beet sugar manufacture, and from the ashes of wood which may contain 15 per cent of potassium carbonate.

Potassium carbonate is a white deliquescent substance very soluble in water: 100 grams of water dissolve 112 grams of potassium carbonate at  $20^\circ$ . It is used to some extent in the laboratory as a drying agent, particularly in organic chemistry. It is also employed for the manufacture of soft soap; of hard glass (page 779), in dyeing, and as a starting point for the production of many potassium salts. It is used in the laboratory, mixed with sodium carbonate, as *fusion mixture*.

Hot concentrated aqueous solutions of potassium carbonate at temperatures between  $10^\circ$  and  $25^\circ$  deposit crystals of a **trihydrate**,  $\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ ; these crystals at  $100^\circ$  lose two molecules of water, forming the **monohydrate**,  $\text{K}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . The latter become anhydrous at  $130^\circ$ .

**Potassium bicarbonate**,  $\text{KHCO}_3$ , is readily obtained as a white crystalline powder by passing carbon dioxide through a cold saturated solution of the normal carbonate. It is much less soluble than the

latter: 100 grams of water dissolve 27.7 grams of potassium bicarbonate at 10° and 33.2 grams at 20°. It is thus much more soluble than sodium bicarbonate.

### Potassium Chloride, KCl

This salt occurs in large quantities in the Stassfurt deposits either as the mineral *syvite* (principally KCl) or as *carnallite* (mainly  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). Most of the potassium chloride of commerce is extracted from carnallite, and from the waters of the Dead Sea.

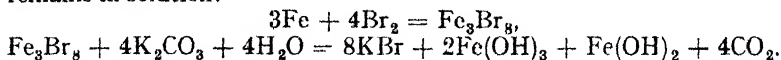
The crude carnallite is crushed and digested in large tanks with the mother liquor left from preceding operations. This liquid contains chiefly magnesium chloride. The mixture is heated by blowing steam into it, when the potassium and magnesium chlorides dissolve, while most of the sodium chloride and magnesium sulphate, associated with the crude carnallite, remain as an insoluble residue. The liquid is allowed to settle for an hour, and then the supernatant liquid is decanted, while still hot, into large iron vats where, on cooling, crystals of crude potassium chloride (contaminated with sodium chloride and a little magnesium chloride) separate. The crystals of potassium chloride are washed with cold water, to remove the more soluble sodium chloride. Further purification, if required, is effected by recrystallization.

This process depends upon the fact that carnallite is only stable in solution in presence of a large excess of magnesium chloride, being otherwise resolved into its constituent salts.

Potassium chloride crystallizes in white cubes like sodium chloride, which it closely resembles in most respects. It is more soluble than sodium chloride in hot water, but less so in cold. Thus 100 grams of water dissolve 28.07 grams of potassium chloride at 0° and 56.3 grams at 100°. It is used extensively as a fertilizer and in the manufacture of caustic potash and other potassium salts.

### Potassium Bromide, KBr

Potassium bromide is made commercially from the crude bromide of iron formed by treating bromine with iron-borings. A solution of this bromide is added to potassium carbonate solution when a mixture of ferrous and ferric hydroxides is precipitated and potassium bromide remains in solution:



The solution is filtered, and the potassium bromide crystallized from the filtrate.

Potassium bromide is thus obtained in white cubic crystals, which are very soluble in water: 100 grams of water dissolve 65.2 grams of potassium bromide at 20°.

It is used extensively in the manufacture of photographic plates,



films and papers, as a constituent of photographic developers and, as a sedative, in medicine.

**Potassium iodide, KI**, is made commercially in a similar manner to that employed for the bromide, which it resembles in many ways. It crystallizes from water in white cubic crystals, which are very soluble in water: 100 grams of water dissolve 144 grams of potassium iodide at 20°.

Potassium iodide is used in volumetric analysis, partly on account of its solvent action on iodine (owing to the formation of the compound  $KI_3$ ), and as a convenient salt from which iodine may be liberated quantitatively by oxidizing agents, so serving for their determination (see page 567). Its solution will also dissolve the iodides of several other metals which are normally insoluble in water. Among these may be mentioned silver iodide and mercuric iodide. The solution of the latter (which contains potassium mercuric iodide,  $K_2HgI_4$ ) is known as **Nessler's Solution** and is used for the detection of minute traces of ammonia, particularly in water analysis. Nessler's solution gives an intense yellow-brown coloration with ammonia. Potassium iodide is also used in photography, and in medicine.

### § 26 Potassium Nitrate, Nitre, Saltpetre, $KNO_3$

Potassium nitrate has been known since quite early times and has for a long period found important applications. Although the sodium nitrate of the Chile nitrate beds had become, until the advent of fixation processes, the principal source of the world's supply of nitrates, potassium nitrate was, and is, preferred for many purposes.

Potassium nitrate occurs as an incrustation on the soil in hot countries, particularly in the neighbourhood of villages (e.g., in India), where the ground becomes saturated with crude sewage. The nitrifying bacteria of the soil (page 444) convert the nitrogenous compounds present into nitrates—principally potassium nitrate, since potassium salts are always present in fertile soil. The "nitre" can be extracted by lixiviation. This process was imitated (e.g., in France during the Napoleonic Wars) by the construction of *nitre beds*.

Most of the potassium nitrate of commerce is made by the action of potassium chloride from Stassfurt on sodium nitrate from Chile. The practicability of this process depends upon the fact that of all the four salts which may be present when hot, saturated solutions of these two are mixed:



the least soluble in the hot mixture will be sodium chloride, which will therefore separate out. If this salt be removed by filtration while still hot, and the filtrate is then cooled to ordinary temperature, the solubility relations are altered and potassium nitrate separates out. The solubility of sodium chloride which might contaminate the nitrate

changes so little with temperature that practically no more separates. These phenomena can be deduced from the solubility curves of Fig. 28.8.

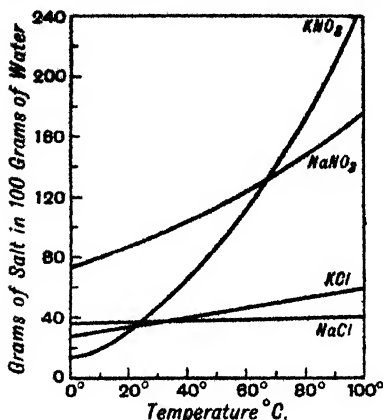


FIG. 28.8.—Solubility Curves of Potassium Nitrate, etc.

The rise of the synthetic nitrogen industry has stimulated attempts to make potassium nitrate without first preparing sodium nitrate. Direct reaction between nitric acid and potassium chloride has been tried; but the formation of nitrosyl chloride is a difficulty to be overcome. Many other methods have been suggested, e.g., using magnesium nitrate (from kieserite and nitric acid); calcium nitrate or ammonium nitrate and potassium chloride.

Potassium nitrate is obtained in white crystals, which are stable in air, easily soluble in hot water but only sparingly so in cold. 100

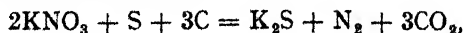
grams of water will dissolve 246 grams of potassium nitrate at 100°, and only 31.6 grams at 20°. On heating, it decomposes like the sodium salt yielding the nitrite. It closely resembles sodium nitrate in chemical properties but, since it is not hygroscopic, it is preferred for such purposes as the production of gunpowder (see below).

The chief use of potassium nitrate is in the manufacture of fireworks and gunpowder. It is also used in pickling meat, and in medicine.

### Gunpowder

Roger Bacon (1214–92) is often credited with the discovery of gunpowder, but there is every reason to believe that he derived his information from an Arabian source. It appears to have been introduced into Europe from the Saracens, and is said to have been first used by the English at the battle of Werewater (1327) and also with memorable effect by Edward III at the battle of Crécy (1346).

Gunpowder consists of a mixture of approximately 75 per cent of potassium nitrate, 12 per cent of sulphur and 13 per cent of charcoal, intimately ground under heavy rollers. When ignited, these materials react with explosive violence, producing a very large volume of gas, so much greater than that of the original materials that if the powder be ignited in a closed space the expanding gases give the mixture the propelling and splitting powers characteristic of explosives. Theoretically, the reaction is represented:



the potassium sulphide remaining as a solid residue, though the

reaction is more complicated than this and side reactions cause other products to be formed, including potassium carbonate and potassium sulphate.

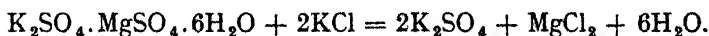
### § 27 Potassium Sulphides and Sulphates

#### Potassium Sulphides

These compounds closely resemble the corresponding sodium derivatives, and can be prepared in a similar way. A substance known as *liver of sulphur*, which was formerly used in laboratory work (e.g., by Cavendish, page 588), is prepared by fusing potassium carbonate with an excess of sulphur, and consists largely of potassium pentasulphide,  $K_2S_5$ , together with smaller quantities of other sulphides, and potassium sulphate and thiosulphate. A solution of liver of sulphur is used as a garden spray against mildew and insects.

#### Potassium Sulphate, $K_2SO_4$

Potassium sulphate occurs in large quantities in various double salts of the Stassfurt deposits, e.g., *schönite*,  $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ , and *kainite*,  $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$ , from which it is prepared. If a hot saturated solution of kainite be allowed to cool, *schönite* separates. This is treated with sylvine (potassium chloride) solution, when the following reaction occurs:



The sparingly soluble, anhydrous potassium sulphate separates first—the mother liquor, on concentration, deposits carnallite (page 640),  $KCl \cdot MgCl_2 \cdot 6H_2O$ , from which potassium chloride (page 640) and magnesium chloride are prepared. Potassium sulphate is also manufactured in small quantities by heating potassium chloride with sulphuric acid and as a by-product in the manufacture of potassium dichromate and potassium permanganate.

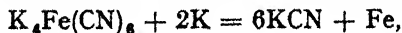
Potassium sulphate crystallizes from aqueous solution in colourless crystals without water of crystallization. It is not very soluble in water: 100 grams of water will dissolve 6.85 grams of potassium sulphate at  $0^\circ$ . It is used for making potash alum, and as a fertilizer, particularly for tobacco and for wheat, in which latter it markedly improves the quality of the straw.

**Potassium bisulphate, potassium hydrogen sulphate,  $KHSO_4$ ,** closely resembles the corresponding sodium salt. It is used to attack refractory minerals for analysis. Small amounts are used in the manufacture of cream of tartar and as a flux in metallurgy.

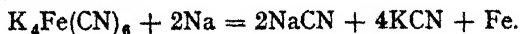
**Potassium cyanide, KCN,** was formerly made by heating potassium ferrocyanide either alone or mixed with potassium carbonate:



but prepared in this way it always contained some potassium cyanate. It can be made by heating potassium ferrocyanide with metallic potassium:



and the mixture of sodium and potassium cyanides resulting from the similar use of metallic sodium in this process has often been sold as potassium cyanide:



### § 28 Detection and Determination of Potassium

Potassium salts impart a characteristic lilac colour to the bunsen flame. This is easily obscured by even small traces of sodium, but if the flame be observed through blue glass the lilac potassium flame can be readily detected.

Potassium can be detected in solution (provided other metals than the alkali metals have been removed) by addition of a solution of platinic chloride in concentrated hydrochloric acid, followed by alcohol, when a yellow precipitate of potassium hexachloroplatinate— $\text{K}_2\text{PtCl}_6$ —indicates the presence of potassium. Perchloric acid (in 20 per cent solution) and alcohol will similarly give a white precipitate of potassium perchlorate. This is a less expensive reagent than platinic chloride, and equally effective as a test. Another sensitive test is the addition of a solution of sodium cobaltinitrite which gives a yellow precipitate of potassium cobaltinitrite,  $\text{K}_3\text{Co}(\text{NO}_2)_6$ .

Like sodium, potassium is usually determined as sulphate, but the chloroplatinate has also been used and more recently the reaction with sodium cobaltinitrite has been applied with success to the determination of potassium.

### § 29 Rubidium and Caesium, Rb and Cs

These two elements, which are closely related to sodium and potassium, are both rare elements. Rubidium is widely distributed, but caesium is extremely rare. Rubidium occurs to the extent of about 1 per cent in the mineral lepidolite (page 607); and carnallite (pages 529, 687) contains about 0.035 per cent of rubidium chloride. Both rubidium and caesium occur in very small quantities in certain mineral waters (e.g., at Dürkheim in the Palatinate). Caesium is found also in the very rare mineral *pollux*, or *pollucite*, a silicate found on the island of Elba.

Both these elements were discovered in 1861 by Bunsen and Kirchhoff by means of the spectroscope. They evaporated down forty tons of the mineral water of Dürkheim, and removed the alkaline earths and lithium by precipitation with ammonium carbonate. Spectroscopic examination of the filtrate gave, besides the lines of lithium, sodium and potassium, two splendid blue lines near the blue strontium line. Since these lines did not correspond with those of any then known element, Bunsen and Kirchhoff concluded that they were due to the presence of a new element and gave it the name caesium (from the Latin *caesius*, blue of the eyes).

Similarly, on extracting the alkalis from lepidolite, and washing the precipitate obtained by treating the solution of the alkalis with hydrochloro-platinic acid with boiling water, they obtained a residue which, when examined spectroscopically, gave, besides those due to strontium and potassium, a number of new lines. Two of these lines lay very far to the red end of the spectrum and hence the new element was named rubidium (from the Latin *rubidus*, dark red).

Both these elements closely resemble potassium. Metallic rubidium has been obtained by heating an intimate mixture of the carbonate and finely divided

carbon. Also by heating the chloride with calcium in an exhausted tube of hard glass. It is softer, more fusible (m.p.  $38.8^\circ$ ), more volatile (b.p.  $679^\circ$ ) and denser (d. 1.53 at  $20^\circ$ ) than potassium. Chemically, it is very similar, but its actions are more vigorous. Like potassium, it exhibits feeble radioactivity, the isotope of mass number 87 emitting  $\beta$ -rays.

Caesium exhibits similar divergence from potassium to a greater degree. Thus, it melts at  $29.7^\circ$ , boils at  $690^\circ$ , and its density is 1.9 at  $20^\circ$ . It is even more vigorous in its chemical activity than rubidium, but is not radioactive. The metal has been obtained by heating the hydroxide with magnesium and by electrolysis a fused mixture of caesium and barium cyanides and, like rubidium, by means of calcium.

A characteristic property of these two elements, in which they differ from the other alkali metals, is in the readiness with which they form stable polyhalides. Among these may be mentioned  $\text{RbBrCl}_2$ ,  $\text{RbClBr}_2$ ,  $\text{RbBr}_3$ ,  $\text{RbICl}_4$ ,  $\text{RbIBr}_3$ ,  $\text{RbI}_3$ ,  $\text{CsClBr}_2$ ,  $\text{CsBrCl}_3$ ,  $\text{CsBr}_3$ ,  $\text{RbICl}_4 \cdot \text{CsI}_3$ . An alloy of caesium and silver is used in the *emivron* or "electric eye" used in television.

The atomic weights of rubidium and caesium were determined by conversion of the chlorides and bromides into silver chloride and bromide. The values at present recommended as the most probable are 85.48 for rubidium, and 132.91 for caesium. The atomic weight of caesium has also been found by the action of silica on caesium nitrate, by which means the ratio  $\text{Cs}_2\text{O} : \text{N}_2\text{O}_5$  can be found.

### § 30 Element No. 87. Francium

There was a gap in the Periodic Table between radon and radium, indicated clearly by the atomic numbers of the neighbouring elements. This missing element was expected to be an alkali metal of high atomic weight and possibly radioactive.

Many claims have been made for the discovery of this element but none was substantiated until Perey (1946) showed that element No. 87 arises from the radioactive decay of actinium-227. This decays in two ways; 1.2 per cent goes to element No. 87 (actinium K) by an  $\alpha$ -ray change; the remainder to thorium-227 by a  $\beta$ -ray change. The element, to which the name francium has been given, is radioactive with a half-life period of only 21 minutes. This fact, combined with the small proportion of actinium-227 atoms which yield it, explains the difficulty of detecting its existence.

## CHAPTER 29

# COPPER, SILVER AND GOLD

The properties of an element in two different states of oxidation differ absolutely from one another; and in these two states the element appears in two entirely different roles.—J. LOCKE.

The extensive use of this metal wherever gorgeous ornament is required, as well as in the simplest designs of art—from the glittering crown of an emperor to the neat little wedding ring of the village maid—has imparted to gold an interest which other metals have failed to excite.—H. SOWERBY.

### § 1 Copper, Cu. History and Occurrence

#### History

COPPER appears to have been known from prehistoric times—the Neolithic Age—long before the histories of the ancient peoples were engraved on stone pillars or inscribed on papyri. The “copper age” followed the “stone age.” At the time of Rameses II (about 1300 B.C.), copper was so costly that it was stored among the treasures of Egyptian temples. Copper appears to have been used for making utensils and instruments for war before iron. This is probably owing to the fact that copper occurs native in a form requiring no metallurgical treatment. The ancients used the terms *χαλκός* (*chalcos*) and *aes* for copper, brass, and bronze. In fact, the terms for copper, brass, and bronze are much confused by the old writers, e.g., Pliny, showing that they did not understand the difference. Pliny wrote a celebrated *Natural History* at the beginning of this era. In this book he laboriously garnered what he could of facts and fable then known concerning nature; hence the book is often quoted. Copper was afterwards called *aes cyprium* (i.e., Cyprian brass), since the Romans first obtained it from the Isle of Cyprus; the term *aes cyprium* was soon abbreviated to *cuprum*. Hence the modern symbol “Cu.”

#### Occurrence

Metallic copper is found in many localities; e.g., considerable masses have been found in Michigan, on the shores of Lake Superior; and small quantities in many other places—Cornwall, Siberia, Ural, Australia, Chile, etc. Compounds of copper are distributed in nature as oxide in *cuprite*, or ruby ore,  $\text{Cu}_2\text{O}$ ; as sulphide in *chalcocite*, or copper glance,  $\text{Cu}_2\text{S}$ ; copper pyrites or *chalcopyrite*,  $\text{CuFeS}_2$  or  $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ . The real composition of many copper sulphides, as they occur in nature, is exceedingly complex. The same remark is more or less true for the composition of most natural minerals; at least chemical formulae which follow the analyses closely are very complex. **The formulae for minerals**

re commonly represented as if pure minerals occurred in nature. Ideally pure minerals very seldom occur in nature, and accordingly, the formulae represent ideal or imaginary minerals to which real minerals approximate more or less closely. Copper also occurs in many places as basic carbonate, *malachite*,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ; and *azurite*,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . *Bornite*,  $\text{Cu}_3\text{FeS}_3$  (or  $3\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ ) and *atacamite*,  $\text{CuCl}_3 \cdot 3\text{Cu}(\text{OH})_2$  also occur in some quantity. Copper silicates, arsenates, phosphates, etc., are also known to occur. Copper has also been found in the feathers of some birds and in the blood of a shore crab on the New England coast of the U.S.A.

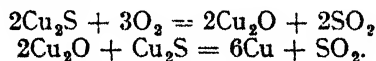
## § 2 Manufacture of Copper

The principal source of copper is copper pyrites, which contains varying amounts of copper and iron sulphides, though a good deal is obtained from the deposits of native copper on the shores of Lake Superior, etc.

The method depends upon the fact that ferrous sulphide is more readily oxidized than cuprous sulphide and will also react with cuprous oxide to form ferrous oxide and cuprous sulphide



Consequently, when a mixture of these two sulphides is roasted in air ferrous oxide is formed in preference to cuprous oxide and any cuprous oxide present is converted into cuprous sulphide. Silica (usually in the form of quartz) is added and the ferrous oxide reacts with it to form a slag. This slag floats on the surface of the cuprous sulphide and is removed. The cuprous sulphide will then react with more air and yield the metal by autoreduction:



The actual operation is carried out in stages:

1. Concentration of the ore by flotation.
2. Roasting of the ore.
3. Smelting (production of *matte*).
4. Conversion of *matte* to *blister copper*.
5. Refining of blister copper.

### 1. Concentration of the Ore

This is effected by grinding the ore to a fine powder, after which the metal-bearing particles are separated from the gangue, etc., by agitation with water and suitable reagents, so that the froth so formed carries with it a desired constituent of the original ore. The froth is made to overflow and is collected. In this way, quite low-grade ores, which could not formerly be smelted economically, are now concentrated up to 25 per cent of copper.

## 2. Roasting the Ore

The ore is next roasted in a furnace consisting of a vertical tier of nine or more circular hearths. Each hearth is provided with a rotating raking device and the whole furnace is so arranged that the ore charged on to the top hearth gradually moves down the furnace from hearth to hearth. No fuel is usually required since the oxidation of the sulphur in the ore furnishes sufficient heat to keep the process going. Copper sulphide, as mentioned above, oxidizes much less rapidly than iron sulphide and the roasting is so adjusted that, when completed, the amount of sulphur still remaining is just sufficient to form cuprous sulphide with all the copper present. The sulphur dioxide may be made into sulphuric acid, or (in the future) will probably be reduced to sulphur (page 490).

## 3. Smelting—Production of Matte

This stage in the process was formerly carried out in blast furnaces but is now done in a reverberatory furnace. The roasted ore, mixed with silica in the form of quartz, is heated in such a furnace. The ferrous oxide formed is converted to slag by the quartz and cuprous sulphide (and possibly a little ferrous sulphide is left). The mixture of copper and iron sulphides melts together to form *matte* and the slag floats on the surface of this. The slag is run off continuously and the molten matte is tipped at intervals into large ladles and conveyed to the converters for the next process.

## 4. Conversion to Blister Copper

The molten matte is run into a converter (similar to the Bessemer converter used in steel manufacture, page 907) lined with magnesite, and an appropriate amount of quartz is added. A blast of air is blown through the melt, oxidizing the sulphur, iron and many other metals (if present). The volatile oxides are driven off and the iron oxides combine with the silica to form a slag. Some of the cuprous sulphide is oxidized to cuprous oxide and the blowing is continued until cuprous sulphide and oxide are present in right amount to bring about auto-reduction (*vide supra*). The progress of the operation can be accurately judged by the appearance of the flame issuing from the mouth of the converter. When the matte is completely converted to copper (and the free copper is beginning to oxidize), the blast is stopped and the copper poured off. As the copper cools, any sulphur dioxide dissolved by the metal is expelled, giving the metal a blistered appearance. Hence the product is known as *blister copper*.

## 5. Refining the Crude Copper

Two methods have been used for copper-refining, viz., roasting in a reverberatory furnace and electrolysis. In the furnace method blister copper is melted in a reverberatory furnace in a stream of air. Any



sulphur left is removed as sulphur dioxide, arsenic volatilizes as the trioxide, and other metals, e.g., iron, form a scale of oxide which is skimmed off. The metal thus purified still contains cuprous oxide, which makes it somewhat brittle, and this is removed by stirring it with a log of green wood, when the hydrocarbons formed, in bubbling through the molten metal, reduce it to copper. The product contains about 99.5 per cent of copper and is known as *tough pitch copper*.

If a metal of very high purity is required (e.g., for electrical purposes) or if gold and silver are present in recoverable quantities the tough pitch copper is further refined by electrolysis. Slabs of crude metal for anodes are suspended between thin cathodes of pure copper in a bath containing about 15 per cent of copper sulphate and 5 per cent of sulphuric acid. When the current is passed, copper dissolves from the anodes, and pure copper is deposited on the cathodes, the net result being the transference of the copper from anode to cathode. The impurities from the anode either pass into solution or are deposited as a slime near the anode (anode mud). Considerable amounts of silver and gold are obtained from the anode mud. Thus American "copper" furnishes 110 oz. per ton of silver and  $\frac{1}{4}$  oz. per ton of gold, a quantity nearly sufficient to pay for the cost of refining. Electrolytic copper is 99.96 to 99.99 per cent pure.

When the copper is to be subjected to electrolytic refining auriferous or argentiferous quartz is often used in the earlier operations since the gold or silver they contain become concentrated in the crude copper and so can be recovered profitably even though the quantities present are too low to be worth working the quartz for them directly.

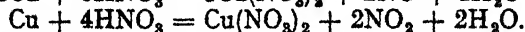
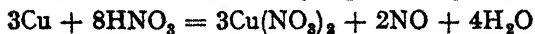
### § 3 Properties of Copper

Copper has a characteristic reddish-brown colour when a clean surface is seen by reflected light; but in transmitted light thin layers are green. It can be obtained in octahedral crystals (cubic system). Copper melts at  $1083^{\circ}$  if heated in an atmosphere of carbon monoxide; in air the melting point is some  $20^{\circ}$  lower owing to the formation of cuprous oxide which dissolves in the molten metal. It is a fairly dense metal, its specific gravity being 8.92 at  $20^{\circ}$ , and it is an excellent conductor of heat and electricity. The molten metal mixes readily with many other metals forming alloys (see below).

Copper does not burn in air, but is gradually converted into cuprous ( $\text{Cu}_2\text{O}$ ) and cupric ( $\text{CuO}$ ) oxides on its surface when heated to redness. The finely divided metal will burn in chlorine or sulphur vapour. It does not react with steam at any temperature below white heat, and then only to a very slight extent. Copper is below hydrogen in the electrochemical series (page 231) and hence does not react with acids unless they are also oxidizing agents, or form complex ions with copper. It is, however, also slowly attacked by some acids in presence of air, owing to the slow oxidizing action of the air.

Although unaffected by *dry* air at the ordinary temperature, exposure to moist air causes the formation of a beautiful green coating or patina. This was for long said to be a basic copper carbonate, but Vernon and Whitby (1929) have shown that it is, in inland places, a basic sulphate— $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ , while near the sea this is accompanied by a basic chloride— $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ .

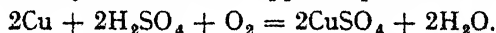
Copper reacts readily with nitric acid, oxides of nitrogen being formed. With the dilute acid (equal volumes of the ordinary concentrated acid and water, equivalent to 40–45 per cent of  $\text{HNO}_3$ ), nitric oxide (along with a little nitrogen peroxide) is formed (cf. page 459), while with the concentrated acid nitrogen peroxide predominates:



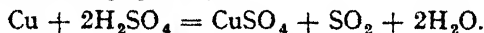
Suggestions as to the mechanism of these reactions are discussed on page 451. It is curious to note, however, that copper is not attacked by nitric acid which has been completely freed from nitrous acid.

Copper is not attacked by dilute hydrochloric acid nor, in absence of air or oxidizing agents, by the concentrated acid even when hot, but in presence of air or with periodic addition of a few drops of nitric acid or a few crystals of potassium chlorate a solution of cupric chloride is readily formed.

Copper is only attacked by dilute sulphuric acid if air is present, and then only slowly; in that case copper sulphate results:

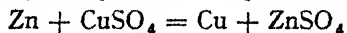


Hot concentrated sulphuric acid readily reacts with copper, sulphur dioxide being evolved (page 487):

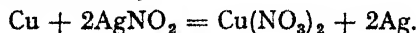


Caustic alkali solutions are without action on copper.

As it is so low in the electrochemical series, copper is displaced from solutions of its salts by many metals—e.g., zinc or iron.



The familiar experiment of dipping a knife blade into copper sulphate solution, with consequent formation of a layer of copper on the blade, is an example of this. Copper will, in its turn, displace silver, gold or platinum from their solutions since these metals are still lower in the electrochemical series, e.g.,



#### § 4 Alloys of Copper

Copper readily forms alloys with other metals and many of these are of considerable importance technically. Table XL (page 651) shows the approximate composition of some of them.

*Bronze* is the name originally given to copper-tin alloys but nowadays the name is used for almost all copper alloys in which resistance to wear is an essential characteristic. Thus manganese bronze is really a high-tensile brass containing a little manganese. Bronzes are tough and tenacious materials. Ordinary bronze is used for making statues, coins, ornaments, etc. Phosphor-bronze is one of the strongest of non-ferrous

TABLE XL.—COPPER ALLOYS

Alloy	Percentage of						
	Copper	Tin	Zinc	Lead	Iron	Nickel	Other elements
Bronze:				sometimes			
Ordinary bronze .	88-96	4-12		0.5			
Gunmetal .	88	10	2	0.5			
Phosphor-bronze .	85	13					P 0.25-2.5
Aluminium-bronze	81.5-90	0-0.5				0-6	Al 7-12
Silicon-bronze .	95-98	2-5					Si 2-5
Lead-bronze .	66-86	4		10-30		sometimes 1	
Beryllium-bronze	97-75						Be 2-25
Bell metal .	80	20					
Manganese-bronze	59	1		up to 40			
Brass:							
Gilding metal .	90		10	0.5 often added			
Alpha or "70 : 30"	70		30				
Alpha-beta or "60 : 40" .	57-63		37-43				
Naval brass .	62	1	37				
Brazing metal .	50		50				
Dutch metal .	80		20				
Copper-lead .	50-70			30-50			
Speculum metal .	66-68	32-34					
German silver .	25-50		25-35			10-35	
Delta metal .	60		38.2		1.8		
Monel metal .	27-28				2-3	70	
Constantan .	60					40	
British copper coinage .	95-95.5	3-4	1-1.5				

metals and is used in bearings, valves, etc., where strength and resistance to wear must be combined with resistance to corrosion. Lead is frequently added to improve the anti-friction and machining qualities. Manganese-bronze is used for the propellers of ships and in machinery generally. Aluminium bronze is a hard, light, yellowish-brown alloy, used for making the hulls of yachts, etc. Silicon-bronze is used for telegraph wires. Copper-cadmium alloys, containing from 0.5 to 1 per cent of cadmium, are used for overhead conductors for electric railways. Copper-beryllium alloys, characterized by high elasticity and resistance to fatigue, are finding increasing use.

*Brass* is a fairly soft alloy and can be readily turned on a lathe or otherwise worked. It is an alloy of copper and zinc. There are many different types of brass but they can be roughly classified as shown in the table. *Gilding metal* is used chiefly for ornament; "70-30" for heavy cold working; "60-40" for hot working. In its various forms it thus finds many uses, e.g., for the manufacture of pins, and for many parts of machinery, and in making musical instruments. *Bell metal* is used in bell-founding, *gunmetal* was formerly used for making cannon and now finds other uses, particularly for engineering purposes such as for gears and bearings. *Speculum metal* is used for optical instruments, and *german silver* for making resistance coils and for imitating silver. *Delta metal* might be described as a brass to which iron has been added, and is characterized by a very high tensile strength. *Monel metal* is a copper-nickel alloy which also has a high tensile strength and, in addition, is very resistant to chemical action so that it is extensively employed in chemical industry (e.g., caustic soda manufacture, page 615). The addition of 0.5 to 1 per cent of tellurium to copper improves its machining qualities to a large extent. This alloy came into prominence during the war (1939-45) in the manufacture of the magnetron.

Copper alloys are extensively used in coinage, and gold and silver used in jewellery are usually alloyed with copper to give them hardness and durability without detracting from their appearance. British copper coins contain 95 per cent of copper, 4 per cent of tin, and 1 per cent of zinc. Some issues since the 1914-18 war have the composition: copper, 95.5 per cent; tin, 3.0 per cent; and zinc, 1.5 per cent. Gold and silver coins usually contain 8 to 10 per cent of copper. British silver coins struck before 1920 contained 7.5 per cent of copper. From 1920 to 1922 they contained 40 per cent of copper and 10 per cent of nickel, later issues had 50 per cent of copper and no nickel. Silver coins minted after 1927 had the composition: silver, 50; copper, 40; zinc, 5; nickel, 5 per cent. The use of silver for coinage ceased in this country at the end of 1946 and all coins minted before that date are being withdrawn. They are being replaced by coins made of an alloy of copper and nickel containing 75 per cent of copper. (Cf. page 666.)

### § 5 Uses of Copper

Next to iron, copper is the most useful metal we have. Enormous quantities are used in the electrical industries, for household utensils and for brewery vessels. Large quantities are used for the fireboxes of locomotive boilers and for steam pipes in stationary plant. Copper nails, rivets and sheeting were used for sheathing wooden ships. As mentioned in the preceding section, it is a valuable constituent of many alloys. Copper is notable in having extensive use in the pure condition; most metals require to have their properties modified by the addition of small quantities of other substances in order to make

them most useful. Many compounds of copper have important uses; these will be mentioned under the heading of the compounds concerned.

### § 6 Atomic Weight of Copper

The atomic weight of copper is shown to be in the neighbourhood of 63·5 by the vapour density of volatile copper compounds, and by the application of Dulong and Petit's rule to the specific heat.

The combining weight has been determined by many methods. The accepted "International" value is 63·54 and depends upon the work of Hönigschmid and Johanssen who synthesized cupric chloride and compared it with silver by precipitation of silver chloride. Their values range from 63·539 to 63·545 in a series of twenty determinations the mean value being 63·542.

### § 7 Copper Hydrides and Oxides

**Cuprous hydride**,  $\text{CuH}$ , is believed to be formed, in an hydrated state, as a red precipitate by the action of hyposulphites (page 514) or of hypophosphites (page 824) on solutions of copper sulphate. It is a very unstable, reddish-brown substance and cannot be kept for any length of time, since it decomposes suddenly, leaving a sponge of metallic copper. A similar, but anhydrous, product results when cuprous iodide is reduced with lithium aluminium hydride in ethereal solution and is almost certainly the hydride  $\text{CuH}$ .

**Cupric hydride**,  $\text{CuH}_2$ , has been reported as an intermediate compound in the formation of cuprous hydride, into which it is supposed to decompose with evolution of hydrogen. The existence of a definite compound,  $\text{CuH}_2$ , is, however, very doubtful.

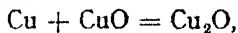
Copper furnishes two oxides whose existence is established, viz.:

Cuprous oxide,  $\text{Cu}_2\text{O}$ ,  
Cupric oxide,  $\text{CuO}$ .

In addition, oxides of the formulae  $\text{Cu}_2\text{O}_3$ ,  $\text{Cu}_3\text{O}$ ,  $\text{Cu}_4\text{O}$  and  $\text{CuO}_2$  have been reported, but the evidence is indecisive.

#### Cuprous Oxide, $\text{Cu}_2\text{O}$

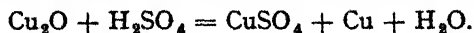
Cuprous oxide is formed when copper or copper oxide is heated to a high temperature, but cannot be prepared pure in this way. It is made either by heating cupric oxide with copper powder:



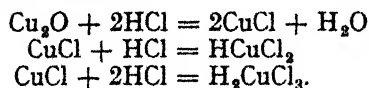
or, better, by the action of glucose on an alkaline solution of a cupric salt. The addition of sodium hydroxide to a solution of copper sulphate causes the precipitation of cupric hydroxide (below, page 655); but if Rochelle salt (sodium potassium tartrate) be first added to the solution, no precipitate results with sodium hydroxide, and a deep blue solution of a sodium potassium cupritartrate is formed in which the copper is present in a complex anion. This deep blue solution is known as

*Fehling's solution.* If to this solution glucose be added and the mixture warmed, the blue colour disappears and cuprous oxide is precipitated as a red powder.

Cuprous oxide is an insoluble red powder. When heated in air it is partly oxidized to cupric oxide; and it is easily reduced to metallic copper by heating in a stream of hydrogen or coal gas. With most acids its behaviour is unusual for, instead of forming a cuprous salt, the corresponding cupric salt results and free copper is deposited, e.g.:



Yet with hydrochloric acid, cuprous chloride ( $\text{CuCl}$ ) is formed, but dissolves in excess of the acid probably because of the formation of complex chloro-cuprous acids:



Nitric acid reacts violently with cuprous oxide, forming cupric nitrate and oxides of nitrogen. It may be that cupric nitrate and copper are first formed and that the free copper then reacts with more nitric acid.

Cuprous oxide is extensively used in the glass industry, since it imparts a deep red colour to glass. It is also employed in preparing anti-rust paints. Red Chinese flambé glazes are produced by developing glazes containing copper oxide in a reducing atmosphere. The colour is probably colloidal copper suspended in the glaze.

### Cupric Oxide, $\text{CuO}$

Cupric oxide or *black copper oxide* can be made by most of the standard methods (cf. page 340). It is prepared in the laboratory by heating the nitrate (obtained from copper and nitric acid), the carbonate or the hydroxide (q.v.).

Commercially it is made by heating *malachite* (the native carbonate); and also from the copper scale, etc., which results from the working of copper in boiler shops, etc. This material, which is a mixture of copper, cuprous and cupric oxides, is treated with a little nitric acid and heated to redness, thereby converting the whole into the oxide.

Cupric oxide is a black powder, not affected by water. It is stable to moderate heating, but at high temperatures ( $1000^\circ$ – $1200^\circ$ ) decomposes into oxygen and cuprous oxide. When heated, it is reduced to the metal by reducing agents, such as hydrogen, carbon monoxide, hydrocarbons, and carbon. It is a typical basic oxide and forms characteristic salts with many acids—the *cupric salts* (pages 659–662).

It is used in glazes and glasses to which it imparts a green or blue colour; probably on account of the formation of copper silicate. It is used in the laboratory in the analysis of organic compounds, the carbon and hydrogen of which it oxidizes to carbon dioxide and water respectively.

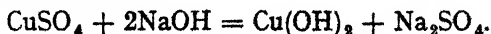
### § 8 Hydroxides of Copper

Theoretically two hydroxides would be expected to exist corresponding to cuprous oxide and cupric oxide respectively.

Actually **cuprous hydroxide** seems not to exist. A yellow precipitate is first obtained in the preparation of cuprous oxide from Fehling's solution (page 653), which rapidly turns into the red cuprous oxide itself. This yellow precipitate has been thought by some to be cuprous hydroxide; but is generally supposed to be a colloidal "mixture" of cuprous oxide and water of no fixed composition.

#### Cupric Hydroxide, $\text{Cu}(\text{OH})_2$

When a solution of sodium or potassium hydroxide is added to a cold solution of a cupric salt, a pale blue, gelatinous precipitate of cupric hydroxide is formed:

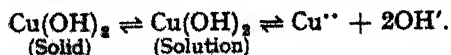


This blue precipitate can be filtered off, but it is very difficult to wash it free from alkali. It can be dried at low temperatures, but on heating to  $100^\circ$  turns black, a substance of the composition  $4\text{CuO} \cdot \text{H}_2\text{O}$  being formed. A similar black substance is obtained if the solution used for preparing the hydroxide be boiled either before or after addition of alkali. Stronger heating removes the remaining water, forming cupric oxide.

Copper hydroxide reacts readily with acids, forming cupric salts, and is also soluble in aqueous ammonia, giving the characteristic very deep blue solution.

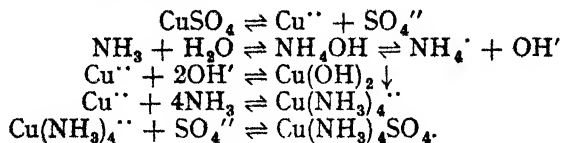
If aqueous ammonia be added to a solution of a cupric salt, cupric hydroxide is first precipitated as with sodium hydroxide, but this redissolves on addition of excess of ammonia, giving a deep blue solution. *Schweitzer's reagent*, formed by adding solid copper hydroxide to concentrated ammonia, dissolves cellulose (e.g., cotton-wool or filter paper). The cellulose is reprecipitated when this "solution" is acidified, and this has been applied in one method for the production of artificial silk. The solution of cellulose in ammoniacal cupric hydroxide solution is squirted through jets into a solution of sulphuric acid (10–50 per cent) or of sodium hydroxide (5–30 per cent), and the cellulose is thus obtained in threads with a silk-like lustre.

The solvent effect of ammonia on copper hydroxide is ascribed to the formation of complex compounds known as **copper amines** or **cuprammonium compounds**, which furnish a complex cuprammonium ion— $\text{Cu}(\text{NH}_3)_4^{++}$ —which is divalent and forms salts with acidic ions. The effect is explained, in terms of the ionic theory, as follows. The precipitated cupric hydroxide is in equilibrium with its own saturated solution, which contains both undissociated hydroxide and its ions:



The ammonia present reacts with the cupric ions, forming cuprammonium ions, thus removing cupric ions from the system and disturbing the equilibrium indicated above. More cupric hydroxide accordingly dissolves and the process continues, provided enough ammonia be present, until all the precipitate has been dissolved.

In the case of the addition of ammonia to a copper sulphate solution, the process may be represented:



Addition of alcohol to the deep blue ammoniacal solution slowly precipitates *copper tetramminosulphate* or *cuprammonium sulphate*,  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , on standing.

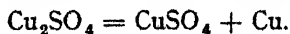
### § 9 Salts of Copper. The Equilibrium between Cuprous and Cupric Salts

Copper forms two series of salts, corresponding to the oxides cuprous oxide and cupric oxide, and known consequently as the cuprous and cupric salts.

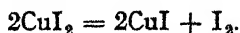
There is still some doubt concerning the true molecular formula of cuprous salts. The vapour density of cuprous chloride corresponds to a formula  $\text{Cu}_2\text{Cl}_2$  even at  $1600^\circ$ . On the other hand, the iodide is  $\text{CuI}$  at  $1000^\circ$  and the freezing points of solutions of cuprous compounds in organic solvents indicate similar differences. The probable conclusion seems to be that univalent copper and the ion  $\text{Cu}^+$  do exist, but that the cuprous compounds have a marked tendency to form double molecules.

Since the electronic structure of copper is 2.8.18.1 the formation of a cuprous ion  $\text{Cu}^+$  leaves a complete shell of 18 electrons so that it is remarkable that the cuprous salts are unstable in solution and become converted into the corresponding cupric salts.

The equilibrium between the cuprous and cupric salts is interesting. The soluble cuprous salts decompose in solution in water into cupric salts and copper, e.g., cuprous sulphate, which can be made in absence of water, decomposes at once in water into cupric sulphate and copper. On the other hand, cupric salts of acids whose cuprous salts are insoluble decompose in water into the cuprous salt which is precipitated, e.g., cupric iodide or cyanide, iodine and cyanogen being evolved also. Thus:



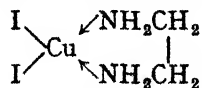
But:



In general, it may be said that cuprous salts cannot exist in contact



with water unless they are either insoluble or combined in a complex. Cupric salts of acids whose cuprous salts are insoluble are similarly unstable in presence of water, but can be sometimes obtained in the form of co-ordination compounds with organic substances, e.g., cupric iodide forms a stable co-ordination with ethylene diamine:

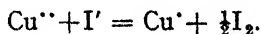


Similar considerations apply to the soluble cuprous salts.

These facts are interpreted in terms of the ionic theory as follows. The interchange between cuprous and cupric salts is represented by the equilibrium:



Hence a soluble cuprous salt will furnish a solution containing much  $\text{Cu}^+$  ion and the equilibrium will tend to move to the right on account of the insolubility of metallic copper. Conversely, when the cupric salt of an acid whose cuprous salt is insoluble is dissolved in water, cuprous ions will be removed by precipitation, and the equilibrium will be moved to the left, but there being only cupric ions (and no free copper) present at the outset, the electron necessary to convert the cupric ion into a cuprous ion is derived from the anion (e.g. the iodide ion):



The stability conferred by the formation of complexes and co-ordination compounds is similarly owing to the removal of, or non-formation of, ions of one or other kind.

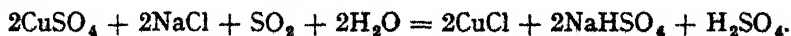
## § 10 Cuprous Salts

### Cuprous Chloride, $\text{CuCl}$

This salt is made by digesting a solution of cupric chloride in concentrated hydrochloric acid with metallic copper (usually in the form of turnings) until the liquid becomes colourless. The solution is then poured into water, when a white precipitate of cuprous chloride separates. It can be filtered off and washed with water containing a little sulphur dioxide to prevent oxidation and dried by means of alcohol and ether, or in a vacuum desiccator:



The reduction of the cupric to the cuprous salt can also be effected by means of sulphur dioxide. Making use of this fact it is sometimes prepared in the laboratory by passing sulphur dioxide through a solution of equimolecular amounts of copper sulphate and common salt:

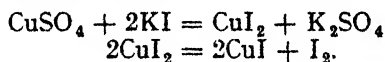


The cuprous chloride is precipitated, and may be filtered off and dried as above.

Cuprous chloride is a white solid, insoluble in water, but soluble in excess of concentrated hydrochloric acid (owing to the formation of complexes such as  $\text{HCuCl}_2$  and  $\text{H}_2\text{CuCl}_3$ ). It melts between  $415^\circ$  and  $422^\circ$ . On exposure to air, it gradually turns green on account of the formation of a basic cupric chloride,  $\text{CuCl}_2 \cdot 3\text{CuO} \cdot 3\text{H}_2\text{O}$ . It dissolves also in ammonia, forming a solution containing  $\text{CuCl} \cdot \text{NH}_3$ . This solution is colourless in the absence of oxygen; as usually prepared in presence of air it is dark blue. Like the solution in hydrochloric acid, it readily absorbs carbon monoxide. Both solutions are employed in gas analysis for the absorption of carbon monoxide. The amount of gas absorbed never exceeds the ratio  $\text{Cu} : \text{CO}$  and it is probable that a compound,  $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ , is formed.

The ammoniacal solution also absorbs acetylene, which reacts with it, forming a precipitate of **cuprous acetylide**,  $\text{Cu}_2\text{C}_2 \cdot \text{H}_2\text{O}$ , a red explosive compound, the formation of which is used as a test for acetylene (cf. page 376).

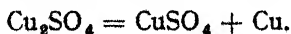
**Cuprous iodide**,  $\text{CuI}$ , is precipitated, mixed with iodine, when aqueous solutions of potassium iodide and of a copper salt (e.g., copper sulphate) are mixed together. It is probable that cupric iodide is first formed, but it is unstable and decomposes as soon as it is formed (cf. § 9):



This reaction is employed in the determination of copper (pages 567, 662), and for separating iodides from chlorides and bromides, since the latter do not give cuprous salts under these conditions.

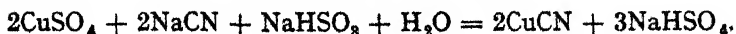
**Cuprous sulphide**,  $\text{Cu}_2\text{S}$ , occurs native as *copper glance*. It is produced when copper is heated with sulphur vapour, when an excess of copper filings is heated with sulphur, and also when copper sulphate solution is warmed with sodium thiosulphate. It is more stable than cupric sulphide which is converted into it when heated to a moderate temperature.

**Cuprous sulphate**,  $\text{Cu}_2\text{SO}_4$ , probably exists, in small quantity, in aqueous solutions of cupric sulphate in contact with metallic copper, but the action must be very slight at ordinary temperatures. In the case of ammoniacal solutions, a colourless crystalline salt,  $(\text{Cu}_2 \cdot 4\text{NH}_3)\text{SO}_4 \cdot \text{H}_2\text{O}$ , has been isolated. Cuprous sulphate can be prepared as a light grey powder by heating together equivalent amounts of methyl (or ethyl) sulphate and cuprous oxide in the absence of moisture. It is decomposed by water into copper and cupric sulphate:



**Cuprous cyanide**,  $\text{CuCN}$ , is formed (analogously to cuprous iodide) on mixing solutions of potassium cyanide and copper sulphate,

cyanogen gas being evolved (cf. page 408); a good method of preparation is by adding a solution of sodium cyanide to a mixture of copper sulphate and sodium bisulphite dissolved in water:



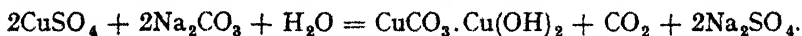
It is a white solid, insoluble in water, but soluble in excess of potassium cyanide forming a stable complex salt potassium cuprocyanide,  $\text{K}_2[\text{Cu}(\text{CN})_4]$ . This property is made use of in the separation of copper from cadmium in qualitative analysis, since the solution does not give the ionic reactions of copper.

### § 11 Cupric Salts

Many cupric salts are soluble in water, yielding blue solutions. Some give green solutions when very concentrated, but go blue when diluted. This behaviour is probably owing to differing degrees of hydration of the cupric ion or to the formation of complexes. Many of the salts crystallize with water of crystallization, forming blue or green crystals. The colour of the anhydrous salts varies considerably. Thus, the anhydrous sulphate is white, the carbonate green, the chloride is brown, and sulphide black.

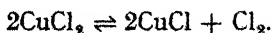
#### Copper Carbonates

Normal cupric carbonate has not been obtained, but two basic carbonates are known. Both occur naturally, and can be prepared in the laboratory. They are *malachite*,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , which is green, and *azurite*,  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , which is blue. The copper carbonate of the laboratory resembles malachite in composition, and is obtained as a fine green powder by mixing solutions of copper sulphate and sodium carbonate:



**Cupric chloride**,  $\text{CuCl}_2$ , can be obtained by dissolving cupric oxide in hydrochloric acid and concentrating the solution, when green crystals of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  separate. The anhydrous salt, which is brown, can be obtained by burning copper in chlorine and allowing the product to cool in presence of chlorine. The salt is soluble in excess of concentrated hydrochloric acid, forming a brown solution which, when diluted, becomes first green and then blue. The green colour is restored on concentration. These changes have been ascribed variously to differences in the degree of hydration of the copper ion; to the formation of complexes, and to the formation of a (supposedly) yellow solution of non-ionized  $\text{CuCl}_2$  which, mixed with the blue ion, would make the solution appear green. The most probable explanation of these colour changes is now thought to be the formation of complex ions in various states of hydration.

On heating to redness, dissociation occurs into cuprous chloride and chlorine:



This was made use of in the now obsolete Deacon process for the manufacture of chlorine.

### Cupric Nitrate, Copper Nitrate, $\text{Cu}(\text{NO}_3)_2$

This salt is most conveniently prepared by dissolving cupric oxide or carbonate in nitric acid and evaporating the solution until very concentrated. Deep blue crystals of the composition  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  are deposited. On heating, the crystals lose water and nitric acid, forming a basic nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ ; and on further heating give off nitrogen peroxide, oxygen, and water, leaving copper oxide behind. The anhydrous salt, which is white, is formed when a solution of nitrogen pentoxide in nitric acid is added to the crystalline hydrate.

### Cupric Sulphide, $\text{CuS}$

This is usually prepared by passing hydrogen sulphide into a solution of a cupric salt (e.g., copper sulphate). It is then obtained as a black precipitate, which is inclined to pass through a filter paper because it is a hydrosol (colloid); it can be coagulated by addition of dilute hydrochloric acid. Cupric sulphide is also obtained as a bluish mass when copper, or cuprous sulphide, is heated with sulphur to a temperature below  $114^\circ$ .

Cupric sulphide is soluble in hot, dilute nitric acid, and in potassium cyanide, forming with the latter a complex— $\text{K}_3[\text{Cu}(\text{CN})_4]$ —from which hydrogen sulphide does not precipitate copper (cf. page 266). Cupric sulphide is insoluble in dilute sulphuric acid (cadmium sulphide is soluble under the same conditions), potassium or sodium sulphides, or ammonium sulphide.

When damp, cupric sulphide is oxidized by the oxygen of the atmosphere to cupric sulphate. When it is heated, either alone or in oxygen, it decomposes into cuprous sulphide and sulphur

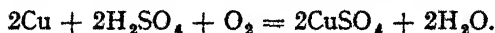


### Cupric Sulphate, Copper Sulphate, Blue Vitriol, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

This is the most important salt of copper and is made commercially on a considerable scale. For this purpose, scrap copper is heated in a reverberatory furnace with sulphur, cuprous sulphide being thus formed. Air is then admitted and the sulphide is oxidized to sulphate. The crude copper sulphate resulting is dissolved in dilute sulphuric acid, insoluble impurities are allowed to settle, and the copper sulphate crystallized out.

It is also made by spraying dilute sulphuric acid on to scrap copper in a lead-lined tower up which air is being blown. The solution so

formed is circulated until a sufficient concentration of copper sulphate is reached.



Copper sulphate is also made by roasting copper sulphide ores so that most of the iron is oxidized. The mass is then digested with "chamber sulphuric acid" (page 498) in which copper oxide dissolves more readily than iron oxide. The small amount of ferrous sulphate which is present in the product so obtained is not objectionable for many of its applications.

Pure copper sulphate is made in the laboratory by dissolving copper oxide in dilute sulphuric acid and evaporating the solution to crystallizing point; followed by further recrystallization if necessary.

As so obtained, copper sulphate forms large, transparent, blue crystals of the pentahydrate— $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ —which belong to the triclinic system. These are readily soluble in water: 100 grams of water dissolve 32.9 grams of the crystals at  $15^\circ$ .

At  $100^\circ$  the blue crystals lose four molecules of water, and the residual monohydrate is bluish white. At  $230^\circ$  white anhydrous copper sulphate— $\text{CuSO}_4$ —is formed. It is very hygroscopic, and turns blue by absorption of water; hence it is used as a test for small amounts of water.

The equilibria among the hydrates of copper sulphate have been considered in Chapter 17 (page 246).

On further heating, it forms a basic sulphate (see below) at  $340^\circ$  and this in turn decomposes into the oxide on very strong heating ( $650^\circ$ – $750^\circ$ ).

Copper sulphate is used extensively for electroplating, in electric batteries, as a mordant in the dyeing and calico-printing trades, for preserving timber and as a fungicide for fruit trees. For this last purpose it is often applied as a solution mixed with milk of lime (Bordeaux mixture). It is also used for the manufacture of green pigments containing copper carbonates.

**Basic copper sulphates** are also known. Thus, by digesting copper sulphate with copper oxide for a long time in air, a yellow powder of  $\text{CuSO}_4 \cdot \text{CuO}$  is formed. This, when thrown into cold water, forms a green insoluble compound,  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ , and in boiling water,  $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ .

The *green patina* which forms on copper sheeting exposed to the weather (e.g., copper roofing) was for long stated to be a basic carbonate. Vernon and Whitby (1929) have shown that it is largely composed of a basic sulphate,  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ . In locations near the sea the corresponding basic chloride is formed.

### Copper Acetates

The *normal acetate*,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , is used in the manufacture of pigments. It is made by dissolving cupric oxide or verdigris in acetic acid.

*Basic copper acetate, verdigris*, is made by placing copper plates in the mass of grape skins and stems left after wine manufacture and which have been allowed to undergo acetous fermentation. When the copper is coated with verdigris, it is exposed to the air for a few days and then immersed again. This is repeated until the whole sheet has been eaten away. The product is *blue verdigris* and is mainly  $\text{Cu}_2\text{O}(\text{CH}_3\text{COO})_2$ . *Green verdigris*, which is chiefly  $\text{CuO} \cdot 2\text{Cu}(\text{CH}_3\text{COO})_2$ , is made by arranging copper plates and cloths in alternate layers, to which air has access, and which are moistened every few days with acetic acid. It is used in paint manufacture, and sometimes in dyeing and calico printing. It is also used for making the very poisonous insecticide and fungicide known as *Paris green* (v. page 839), which is a cupric acetoarsenite.

### § 12 Detection and Determination of Copper

Copper salts in solution are easily recognized by their blue colour, which is rendered more intense by the addition of ammonia. In qualitative analysis, copper is precipitated as sulphide. Copper ferrocyanide (page 200) is also a characteristic copper salt.

Copper can also be detected by means of certain organic reagents (e.g., *cupron*,  $\alpha$ -benzoin oxime, and salicylaldoxime).

When a few drops of a 1 per cent solution of *cupron* in alcohol are added to a slightly ammoniacal solution of a copper salt a green precipitate of  $(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N})\text{Cu}$  is formed. This is a sensitive test for copper. Lead, iron, aluminium, cobalt and nickel do not interfere if a soluble tartrate is also present. This condition may be secured by addition of tartaric acid.

When a solution of a copper salt is made slightly alkaline with sodium hydroxide, and then made acid with a considerable excess of acetic acid a yellowish precipitate of the complex  $\text{Cu}(\text{C}_7\text{H}_5\text{O}_2\text{N})_2$  is formed on addition of 0.5 ml. of a 1 per cent solution of salicylaldoxime. This is an extremely sensitive test, and other elements which might interfere do not do so provided that sufficient acetic acid is present.

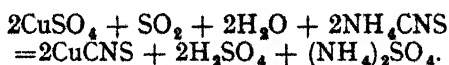
Copper is very conveniently determined volumetrically by addition of excess of potassium iodide solution to a solution containing a known amount of the material to be analysed. The iodine liberated is then titrated with a standard solution of sodium thiosulphate in the absence of any free acid other than acetic. Usually a slight excess of sodium carbonate is added; the excess being removed by addition of acetic acid. Each gram-atom of iodine so found indicates the presence of a gram-atom of copper, e.g.:



(Cf. page 658.)

Copper may be determined gravimetrically by electrolysis on to a previously weighed platinum dish, or by precipitation as sulphide.

The former method is slow though accurate; the latter suffers from the drawback that the ignition of the precipitated sulphide must be carried out in an atmosphere of hydrogen and weighed as cuprous sulphide. A good gravimetric method is by precipitation of cuprous thiocyanate by addition of a slight excess of a 10 per cent solution of ammonium thiocyanate to a solution of the copper salt containing sulphur dioxide:



The precipitate is dried at 110°–120° C. and weighed as the thiocyanate.

The reactions of copper with cupron and salicylaldoxime described above can also be applied to its determination.

### § 13 Silver, Ag. History and Occurrence

#### History

Silver has been known from ancient times. There are some allusions to silver in the Old Testament, and it was probably used as money as early as gold. The Phoenicians are supposed to have obtained their silver from Armenia and Spain. Silver appears to have been purified by a process of cupellation, but there is little evidence to show that the ancients knew how to separate silver from gold. The old terms for silver refer to its bright white colour—the Hebrew equivalent is derived from the verb "to be white," and the Greek term from *ἄργος* (*argos*), shining.

#### Occurrence

Native silver is occasionally found in large masses or crystallized in cubes or octahedra. It is also found associated with metallic copper, gold, etc. The principal ores of silver contain silver glance or *argentite*,  $\text{Ag}_2\text{S}$ , admixed with several other sulphides—antimony, arsenic, and copper. The chief silver ores are found in Mexico, Peru, Chile, Bolivia, Idaho, Arizona, Nevada, Colorado, Norway, Australia, etc. Much silver also occurs associated with lead in galena, and a great deal of the silver in commerce is extracted from argentiferous lead. Silver chloride,  $\text{AgCl}$ , occurs as *kerargyrite*, or horn silver.

### § 14 Extraction of Silver

Many processes have been employed for the extraction of silver, of which may be mentioned:

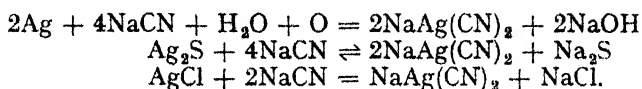
- (i) Cyanide process;
- (ii) Desilverization of lead;
- (iii) Electrolytic process.

The first of these is now the only important method in use for the treatment of silver ores proper; while the second and third are widely

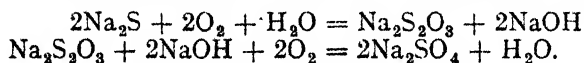
used for the extraction of silver from argentiferous lead and copper respectively.

### Cyanide Process (MacArthur-Forrest)

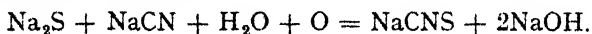
This method depends upon the fact that silver forms soluble complex cyanides with sodium and potassium, so that silver compounds will dissolve in solutions of alkali cyanides. The silver ore, consisting principally of sulphide, is crushed and treated with a solution of sodium cyanide of 0.5 per cent concentration or less, the mixture being agitated by blowing air through it. The silver present passes into solution in the form of sodium argentocyanide by reactions which may be represented by the equations:



The first of these reactions requires the presence of oxygen, the second is reversible and so accumulation of sodium sulphide must be prevented, and this can be secured by its oxidation to thiosulphate and sulphate:

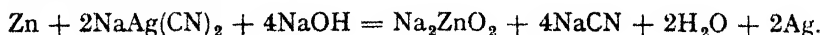


Thus, free access of air to the solution is an important factor in promoting the dissolution of silver. If much sulphide be present some thiocyanate may be formed:



This reaction is avoided, if possible, since it involves loss of cyanide, and in order to prevent it litharge, or lead acetate, is sometimes added. This also assists in the dissolution of the silver by removal of sulphides from the solution.

The silver is recovered, after removal of insoluble impurities, by precipitation with zinc or aluminium. It is important that, at this stage, the solution should be strongly alkaline and so caustic soda is added if necessary:



After separation of the silver the crude mother liquor is used again for the extraction of more of the crude ore. The silver is finally purified by fusion with borax or potassium nitrate.

## § 15 Desilverization of Lead

Two processes have been devised for the desilverization of lead, viz., **Pattinson's process** and **Parkes's process**.

The former is now little used. It depended upon the fact that molten argentiferous lead containing less than  $2\frac{1}{2}$  per cent of silver



(the eutectic amount) deposits crystals of pure lead, which can be removed by means of a perforated ladle. The enriched lead is finally cupelled for silver (see below).

**Parkes's process** depends upon the fact that molten lead and zinc do not mix, but form two layers, the zinc being the upper one. Silver is more soluble in the zinc than in the lead, and further, on cooling, the first portion to solidify is the upper layer, which contains most of the silver. Any gold present also passes into the zinc.

The lead is melted in pots of about twenty-five tons capacity and about 1 per cent of zinc added. The mixture is skimmed frequently as it cools, and the skimmings, consisting of a zinc-silver alloy contaminated with lead, are put into another smaller pot. The contents of this pot are then melted, allowed to cool and skimmed as before. The final skimmings are then distilled with a little charcoal to reduce any oxide present, the zinc being thus recovered, and an alloy of lead and silver remains. The silver is then obtained from this by cupellation (see below). By this process, the silver content of the lead can be reduced to 0.0005 per cent.

### **Cupellation**

This operation has been carried on for over 2000 years. It consists of heating a lead-silver alloy rich in silver, in a stream of air, in a furnace with a shallow flat hearth made of bone ash or cement. The lead is oxidized to litharge  $\text{PbO}$ , which is then partly blown from the surface, and partly absorbed by the bone ash. The end of the process is indicated by the "flash" when the clear surface of the pure melted silver appears.

### **§ 16 Electrolytic Process for Silver**

This is principally a process for the refining of crude silver, though the recovery of silver from crude copper in the electrolytic refining of the latter metal (page 649) is an example of the extraction of silver by electrolysis.

In the electrolytic refining of silver the electrolyte consists of silver nitrate solution with 1 per cent of free nitric acid. A slab of impure silver is used as anode and a plate of pure silver as cathode. Silver is deposited on the cathode, copper dissolves, and gold, if present, is deposited as a slime. The copper present in solution must not be allowed to exceed 4 to 5 per cent.

### **§ 17 Properties of Silver**

Silver is a white lustrous metal which appears yellow if the light be reflected from its surface many times before it reaches the eye. Very thin layers of silver have a bluish tint. Powdered silver is grey and earthy in appearance. Silver is highly malleable and ductile. Sheets

0.00001 in. thick have been made. Silver melts at  $960.8^{\circ}$  in an atmosphere of carbon monoxide, and vaporization commences about  $850^{\circ}$  and proceeds rapidly between  $1200^{\circ}$  and  $1500^{\circ}$ . It boils at  $2193^{\circ}$ . It can be distilled in the oxy-hydrogen blowpipe, or in the electric furnace. The vapour appears of a greenish colour. Molten silver absorbs oxygen, and rejects most of it on cooling. The evolution of oxygen from cooling silver is often violent enough to spurt some of the metal away from the main mass—hence the term *the spitting of silver*. Silver conducts heat and electricity better than copper. Exposure to the air has no action on silver, but if the air be contaminated with hydrogen sulphide, the silver is blackened owing to the formation of a thin film of silver sulphide on the surface. Nitric acid—hot or cold, dilute or concentrated—readily attacks the metal, forming silver nitrate. Hot concentrated sulphuric acid gives silver sulphate, but the metal is not perceptibly attacked by the dilute acid. Hydrochloric acid acts very slowly, if at all, at ordinary temperatures, but at a red heat, hydrogen chloride forms silver chloride. The vapour density of silver vapour at  $2000^{\circ}$  shows that at this temperature the molecules are monatomic.

### Colloidal Silver

By the action of certain reducing agents on soluble silver salts, strongly coloured solutions of colloidal silver have been obtained. Very pure materials are required, and the solution must be kept accurately neutral otherwise coagulation is liable to occur. Colloidal silver, stabilized by the addition of albumen, has been used in medicine as a germicide.

### § 18 Uses of Silver

Metallic silver is widely used in coinage, and for the manufacture of table ware and ornaments. It is too soft for these purposes in a pure condition and is, therefore, alloyed with other metals such as copper. British silver coinage before 1919 contained 92.5 per cent of silver. In 1920 the percentage of silver was reduced to 50, the remaining constituents being from 1920 to 1922, 40 per cent copper and 10 per cent nickel; from 1922 to 1927, 50 per cent copper. The composition of coins struck since 1927 has been: silver, 50 per cent; copper, 40 per cent; nickel, 5 per cent; and zinc, 5 per cent. At the end of 1946 it was decided to give up a silver coinage entirely and replace it by one made of a cupro-nickel alloy containing 75 per cent of copper. All silver coins are now being withdrawn from circulation in this country so that before long the debasement of our coinage will be complete.

Various compounds of silver are used extensively, e.g., in photography (page 672), in medicine, the making of marking ink, and in the laboratory silver and silver nitrate are very important analytical materials. Large quantities of silver are also employed in electroplating, and in the manufacture of mirrors.

### § 19 Atomic Weight of Silver

The atomic weight of silver is of fundamental importance, since it is by way of silver that the atomic weights of most other elements have been determined (cf. pages 104–8). The best determinations so far are believed to be those of Richards, whose value 107.88 is the one at present accepted. Richards's methods are described on pages 105–8, (Chapter 7).

### § 20 Oxides of Silver

The electronic configuration of the silver atom being 2.18.18.18.1 it would be expected that silver would be predominantly univalent in its compounds and this is found to be the case. But, as with copper, one electron from the penultimate shell can be used for valency purposes and so some bivalent compounds of silver (referred to as argentic compounds) are known.

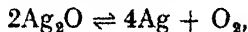
Silver forms two oxides, viz.:

Argentous oxide, Silver oxide,  $\text{Ag}_2\text{O}$ ,  
Argentic oxide,  $\text{AgO}$ ,

while a third, silver sesquioxide,  $\text{Ag}_2\text{O}_3$ , has also been reported, but its existence is still doubtful.

#### Silver Oxide, $\text{Ag}_2\text{O}$

When sodium or potassium hydroxide solution is added to a solution of silver nitrate, a brown precipitate is formed. This might be expected to be silver hydroxide,  $\text{AgOH}$ , but it is believed that this does not exist and that the precipitate is silver oxide (possibly partially hydrated). It is slightly soluble in water (0.05 gram of oxide will dissolve in 1 litre of water at ordinary temperatures) and the solution has an alkaline reaction and a metallic taste. On heating in air to about  $300^\circ$  it decomposes, leaving metallic silver. At lower temperatures (below  $120^\circ$  in air), silver is slowly oxidized, so that the reaction,

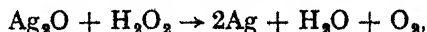


is reversible. At ordinary temperatures the reaction is imperceptible. Application of the phase rule to the system indicates that it will resemble the decomposition of calcium carbonate by heat (cf. page 244) since two solid phases and one gaseous phase are involved. The partial pressure of oxygen in air is about 152 mm., and the dissociation pressure of silver oxide has this value at about  $121^\circ$ . Hence, above this temperature, in air, the oxide will decompose; below it, the metal will slowly oxidize.

Silver oxide is soluble in excess of aqueous ammonia, owing to the formation of the complex ion  $[\text{Ag}(\text{NH}_3)_2]^+$ . (Cf. pages 266 and 434.) On standing, the solution deposits black shining crystals of "fulminating

silver"—an explosive substance the exact nature of which is not known. It may be *silver nitride*,  $\text{Ag}_3\text{N}$ , or the *imide*,  $\text{Ag}_2\text{NH}$ .

Silver oxide is "reduced" by hydrogen peroxide to metallic silver,



and it rapidly oxidizes sulphur, phosphorus, etc., often with incandescence.

#### Argentio Oxide, $\text{Ag}_2\text{O}$

The oxidation of silver oxide by means of hot alkaline potassium permanganate solution or sodium hypochlorite solution yields a dark grey substance which is probably composed mainly of argentic oxide. It is doubtful, however, if this substance has yet been obtained quite pure. It has been supposed that this compound is a peroxide and it has been formulated  $\text{Ag}_2\text{O}_2$  in support of this view but, in its reactions, it does not behave like a true peroxide and so the simpler formula,  $\text{Ag}_2\text{O}$ , is to be preferred.

### § 21 Salts of Silver

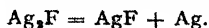
Most of the salts of silver are insoluble, or at least only sparingly soluble, in water, even those of some strong acids, e.g., sulphate and chloride. The only common soluble salts are the nitrate, chlorate, perchlorate and fluoride. (The anomalous solubility of silver fluoride has already been referred to—page 527.)

The formation of characteristic silver salts is made use of in qualitative analysis for the identification of acid radicals. Many silver salts are acted upon by light, a property, first recorded by Gesner (1565), which finds application in photography. (See page 672.)

**Silver carbonate**,  $\text{Ag}_2\text{CO}_3$ , is obtained as a faintly yellow precipitate on mixing solutions of silver nitrate and a soluble carbonate. It is readily decomposed on heating, yielding first the oxide and then the metal.

**Silver fluoride**,  $\text{AgF}$ , obtained by evaporating *in vacuo* a solution of silver oxide in hydrofluoric acid, is chiefly noticeable in being the only halide of silver which is readily soluble in water: 100 grams of water at  $15^\circ$  dissolving 182 grams of silver fluoride.

**Silver subfluoride**,  $\text{Ag}_2\text{F}$ , has been obtained as a bright yellow, crystalline solid by heating a solution of silver fluoride with silver powder or by electrolysis of a solution of the ordinary fluoride. It is unstable above  $90^\circ$  and in contact with water is converted into silver fluoride with deposition of metallic silver:

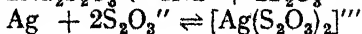
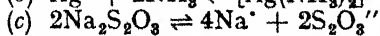
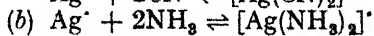
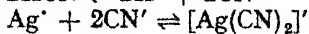
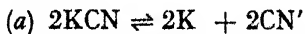
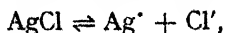


**Silver difluoride**,  $\text{AgF}_2$ , can be made by the action of fluorine on silver or silver chloride or silver fluoride at a temperature of  $150^\circ$  to  $250^\circ$  and is used in organic chemistry for the fluorination of hydrocarbons.

#### Silver Chloride, $\text{AgCl}$

Silver chloride occurs in nature as the mineral *horn silver*. It is formed when a solution of a soluble chloride is added to a solution of a silver salt. A white flaky or curdy precipitate is thus formed which

melts at  $455^\circ$  to a yellow liquid, and which solidifies on cooling to a tough horny mass. Silver chloride is virtually insoluble in water: its solubility has been estimated at 1.5 milligrams in a litre of water at  $20^\circ$ . It is, however, easily soluble in solutions of ammonia, potassium cyanide, and sodium thiosulphate. This behaviour is analogous to that of the copper salts described on pages 434, 655, and is explained in terms of the ionic theory as owing to the formation of complex ions:



It is supposed that the complex ion in each case is in equilibrium with such very small concentrations of silver ion that the solubility product (page 262) of silver chloride is not exceeded. In support of this theory, definite complex compounds,  $\text{Ag}(\text{NH}_3)_2\text{Cl}$ ,  $\text{KAg}(\text{CN})_2$  and  $\text{Na}_2\text{Ag}(\text{S}_2\text{O}_3)_2$ , have been isolated.

Silver chloride is otherwise rather unreactive. Like many other silver compounds, it is affected by light (see below), and like them also, absorbs ammonia gas, forming such ammines as  $\text{AgCl} \cdot 2\text{NH}_3$  and  $\text{AgCl} \cdot 3\text{NH}_3$ . It can be reduced to silver by heating in a current of hydrogen; by fusion with sodium or potassium carbonate, or by contact with zinc in presence of dilute acid. It is converted into silver bromide or iodide when left in contact with solutions of potassium bromide or iodide. This is owing to the fact that the solubility products of the bromide and iodide are much smaller than that of the chloride. Thus, the solubility products of these three salts at ordinary temperatures are:

Silver chloride,  $1.2 \times 10^{-10}$ ; silver bromide,  $3.5 \times 10^{-13}$ ; silver iodide,  $1.7 \times 10^{-16}$ .

Silver chloride is used in photography for the manufacture of printing-out papers.

**Silver bromide**,  $\text{AgBr}$ , is a pale cream solid which resembles the chloride, and is obtained in a similar way. It does not absorb gaseous ammonia, in which it differs from the chloride and iodide. It is soluble in concentrated aqueous ammonia but not in the dilute solution. It is very extensively used in photography for making the sensitive emulsion for plates and films.

**Silver iodide**,  $\text{AgI}$ , is a pale yellow crystalline solid which absorbs gaseous ammonia, but which is scarcely soluble in aqueous ammonia. It is interesting in that it contracts on heating and expands on cooling. It is soluble in concentrated solutions of potassium iodide. Silver iodide is used, along with the bromide, in the making of photographic plates and films.

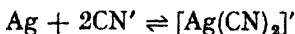
**Silver Nitrate,  $\text{AgNO}_3$** 

Silver nitrate is usually obtained by the action of nitric acid on the metal. On crystallizing the solution, it is obtained in colourless rhombic plates. It melts at  $212^\circ$  and on cooling solidifies to a fibrous crystalline mass called *lunar caustic*. Silver nitrate is readily soluble in water: 100 grams of water dissolve 122 grams of the salt at  $0^\circ$  and 952 grams at  $100^\circ$ . Both the aqueous solution and the solid oxidize organic matter, being reduced to silver which is deposited in a black, finely divided metallic form, especially in light. This property explains its use in medicine, for the treatment of warts, etc., and for marking linen. On heating to  $450^\circ$ , silver nitrate decomposes into **silver nitrite**,  $\text{AgNO}_2$ ; and this at higher temperatures is further broken down to metallic silver and oxides of nitrogen. Silver nitrate is used on a large scale for the preparation of the silver halides required for making photographic plates, films, etc.

**Silver sulphide**,  $\text{Ag}_2\text{S}$ , occurs native. It is a black substance which can be made by precipitating it from solutions of soluble silver salts by means of hydrogen sulphide. It is insoluble in ammonia, in sodium thiosulphate and dilute acids, but is soluble in potassium cyanide solutions, particularly in the presence of air (cf. page 664). The tarnishing of silver articles, when exposed to the air of towns, etc., is owing to the formation of a very thin layer of silver sulphide.

**Silver sulphate**,  $\text{Ag}_2\text{SO}_4$ , is obtained by heating the finely divided metal with concentrated sulphuric acid; or by mixing strong solutions of silver nitrate and a soluble sulphate, when it is precipitated. It is sparingly soluble in water: 100 grams of water dissolve only 0.77 gram of the salt at  $17^\circ$ .

**Silver cyanide**,  $\text{AgCN}$ , is formed as a white insoluble powder when potassium cyanide solution is added to a solution of a soluble silver salt. This precipitate is soluble in excess of potassium cyanide (cf. page 664), and this solution is employed in electroplating. Its use for this purpose, in preference to salts such as silver nitrate, is owing to the fact that it has been found that, in order to obtain a coherent deposit, the solution used must have only a low concentration of silver ion. In the solution of potassium argento-cyanide, this condition can be secured without reducing the conductivity of the solution unduly since the equilibrium



lies far over to the right-hand side, the concentration of  $\text{Ag}'$  ion being thus very low. On electrolysis this ion is discharged at the cathode, the maintenance of the equilibrium keeping the concentration of silver ion at a constant low value.

## § 22 Detection and Determination of Silver

Silver is readily detected in solution by the formation of insoluble silver chloride on the addition of hydrochloric acid. Lead and mercurous chlorides are the only others which are insoluble in these conditions. Lead chloride may be removed, if present, by boiling water, in which it is soluble; and silver chloride can be separated from mercurous chloride since it is soluble in ammonia solution, from which it can be reprecipitated by acidification with nitric acid.

Silver is determined gravimetrically in a similar way. The silver chloride precipitated is filtered off, washed, dried at  $110^{\circ}$ – $140^{\circ}$  and weighed.

Volumetrically, the same process may be used, the end point being determined when another drop of chloride solution causes no further turbidity in the supernatant liquid after the silver chloride precipitate has settled. Alternatively, the end point may be detected (provided the solution is not acid and does not become so in the process of titration) by using a few drops of potassium chromate solution as indicator. When an excess of silver ions is present, red silver chromate is formed, otherwise the solution is pale yellow. This is because the solubility of silver chloride is much less than that of silver chromate and so it is precipitated first. Since at the end point, using the usual notation

$$[\text{Ag}^+] = [\text{Cl}^-]$$

the concentration of potassium chromate should be such that the solubility product of silver chromate is exceeded as soon as this occurs. Recently, certain dyes, such as fluorescein and eosin, and dichloro-fluorescein, have been introduced for use as indicators in this reaction. They become adsorbed on the precipitate and so impart their colour to it when no more chloride ions are present in the solution. When a solution of a chloride is titrated with silver nitrate solution the precipitate adsorbs chloride ions while these are in excess and it will now hold by a secondary adsorption oppositely charged ions present in the solution, e.g., sodium ions. When the end point has just been passed silver ions are in excess and these will be now adsorbed by the precipitate instead of chloride ions and secondary adsorption will attach nitrate ions. But if fluorescein be present in the solution, the fluorescein ion, which is negatively charged and is more strongly adsorbed than the nitrate ion, will react with the first trace of excess of silver ions on the surface of the precipitate, thus turning it red owing to the formation of silver fluoresceinate. The solution, which contains fluorescein ions, is a greenish-yellow colour.

Another volumetric process is known as the **Volhard method**. This depends upon the fact that a solution of silver nitrate when mixed with a solution of potassium thiocyanate gives a precipitate of white silver thiocyanate— $\text{AgCNS}$ . If a few drops of a solution of a ferric salt (iron alum is usually employed) be added to the silver solution, the

appearance of the blood-red colour of ferric thiocyanate (cf. page 928) indicates that all the silver has reacted and so marks the end point of the titration.

### § 23 Photography

The action of light on the halides of silver has been referred to above. Thoroughly dried and purified silver chloride can be exposed to sunlight for several hours without darkening, but if a trace of moisture be present, the chloride darkens, assumes a violet tint and finally turns black. It is now thought that this is owing to the decomposition of silver chloride into its elements; but this is a reversible reaction since, if the darkened chloride be exposed to the action of chlorine in the dark, the chloride is regenerated. Silver bromide and iodide behave similarly.

This sensitiveness of the halides of silver to the action of light is applied in photography. A glass plate or film of celluloid is coated with an emulsion of silver bromide (mixed with a little iodide) in gelatine. (The size of the particles of silver halide has been found to determine the speed of the plate.) The plate is placed in the camera and *exposed* by focusing the image of the object to be photographed on to the plate for a short time. The silver halide granules are affected by the light, and minute nuclei of silver are formed, the most intense change occurring where the light was brightest. No visible change is apparent until the plate is *developed*, i.e., treated with a reducing agent such as pyrogallol, but the plate is now said to possess a *latent image* which is made visible by the process of development which continues the change begun by the light, but is without action on the unexposed parts of the plate. As a result of the action of the developer, finely divided silver is deposited on the parts of the plate illuminated by the light reflected from the object. The deposit is thickest where the light was most intense. Hence, the dark parts of the object appear lightest on the plate, and the light parts dark. The image is thus the reverse of the object, and the plate is accordingly called a *negative*. The silver salt which has not been affected by the light nor by the developer is now removed, and the image thus *fixed* on the plate by immersing the plate in a solution of sodium thiosulphate. The plate is then washed and dried. A *print* is made by laying the negative upon sensitized printing paper—that is, paper prepared in a similar way to the original paper (but silver chloride is usually employed for printing-out paper)—so that the light must pass through the negative before striking the paper. The negative absorbs the light in proportion to the thickness of the deposit of silver, so that the print has the same shading as the object. The paper is then treated with a solution of sodium thiosulphate to fix the image. The print may be *toned* by immersing it in a solution of gold chloride so that some of the silver is replaced by gold; this gives the print a warm reddish tone; if a platinum salt be used instead of gold, a steel-grey tone is produced. The image



on the print will be the reverse of that on the negative, and will therefore correspond with the object. Hence the print may be called the *positive*.

Gaslight and "bromide" papers are exposed and developed in the same way as the plates or films used in making negatives, and use silver bromide as the principal constituent of the emulsion. Self-toning papers contain gold salts incorporated in the emulsion, and so fixing and toning occur simultaneously when the emulsion is wetted.

The way in which the nuclei of silver are formed by the light and make the grains in which they occur developable has been the subject of many theories and much investigation. The precise mechanism has still not been proved beyond doubt but there is now general agreement on the main features of the process. It was shown by Sheppard (1925) that the sensitivity of photographic emulsions is caused by the presence of minute traces (of the order of 1 in 100,000) of organic sulphur compounds in the gelatine used. It is believed that in the process of *ripening* of the emulsion during manufacture (i.e., keeping it warm for a carefully controlled period) minute specks of silver sulphide are formed on the surface of the grains of silver halide. The action of light on silver halides is known to produce electrons, the number of electrons liberated being proportional to the number of quanta (page 147) of light absorbed. These electrons are believed to be trapped by the specks of silver sulphide which then attract interstitial silver ions from the body of the grain of halide. The generally accepted view of the development (i.e., reduction to silver) of the rest of the grain on which specks of silver have been formed by the light and not of the others is that the difference is a consequence of a different *rate* of reduction, the reaction being catalysed by the silver speck, but the precise way in which the catalyst works is still being debated.

## § 24 Gold, Au. History and Occurrence

### History

"Gold," said T. Bergman, "occurs in the bowels of the earth native, possessing a complete metallic form, although in general the small particles of it are so interspersed in various matrices that they are entirely invisible." Gold must have been one of the earliest of metals to attract the attention of primitive man, since it occurs free as **virgin gold** in nature, and is found in the rocks and gravels of many rivers. Flint daggers with gilt handles have been reported from excavations in Egypt, and gold is mentioned in the earliest writings of civilized man. Representations of quartz-crushing and gold-refining processes are reported to have been found in Egyptian tombs dated 2500 B.C.; similar remarks apply to a map showing the gold-mining regions 1350-1330 B.C. The gold mines of Nubia were worked extensively by the early Egyptians. Pliny described the amalgamation process for the extraction of gold. Cupellation processes for the purification of gold were described in the second century, and the same process is probably referred to by Jeremiah in the Old Testament, 600 B.C.

### Occurrence

Gold is generally found in a metallic condition in quartz veins as **reef gold**; and in alluvial gravels as **alluvial gold**—the latter represents

the debris from the weathering of auriferous rocks which has been washed into river beds, etc. Large nuggets are occasionally found—one from California weighed over 190 lb.; and one from Victoria, 183 lb. Native gold is never found pure, but specimens of 99 per cent purity are sometimes found; and one from Cripple Creek (Colorado) was reported to be 99.9 per cent purity.

Metallic gold is very widely distributed in nature in quantities too small to be profitably extracted. Sea-water, for instance, was said to contain about  $3\frac{1}{2}$  grains per ton, but the failure of an attempt, by Haber, to extract it in 1923, suggests that the quantity is much less than this and that this figure was the result of inaccurate assays. Granite, on the average, has about 0.37 part per million; sandstones, 0.03 part per million; limestones, 0.007 part per million. Gold also occurs in small quantities in clays, iron pyrites, and in almost all silver, copper, bismuth, lead, zinc, tellurium, and antimony ores. Gravels which need not be crushed can sometimes be profitably treated for gold—alluvial gold—if but 2 to 3 grains per ton be present, that is, one part of gold per 5 million parts of worthless material. The mean of the returns for the Rand is something less than half an ounce of gold per ton of material treated.

### § 25 Extraction of Gold

Gold is separated from alluvial gravel by mechanical washing; but that found in (auriferous—gold-bearing) quartz is extracted by a cyanide process similar to that employed for silver (q.v. page 664).

#### Washing Processes

The specific gravity of gold is so much greater than that of the associated materials that, when the mixture of sand and gravel is agitated with water in large pans or "cradles," and the rocky matters floated off, the fine particles of gold remain on the bottoms of the cradles as "gold dust"—**panning** or **pan washing**. This primitive method of washing has been replaced by **placer mining**, in which the sand containing the gold is agitated in sluices, that is, in long flumes or troughs with transverse cleets along the bottom, and through which powerful streams of water flow. The water sweeps away the sand, and the heavier gold collects on the bottom of the sluices. In **hydraulic mining**, water under high pressure is directed against the "earth" containing the gold. The "earth" and gold are washed into the sluices as in placer mining.

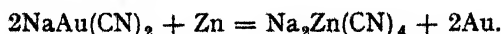
#### Cyanide Process

The gold-bearing quartz is mined by blasting, crushed to a very fine powder in stamp mills and a pulp of the ground ore and water made alkaline with slaked lime. The mixture is then agitated with a dilute aqueous solution of sodium cyanide (0.03 to 0.08 per cent),

whilst freely exposed to atmospheric air. The gold slowly reacts with the cyanide, forming sodium aurocyanide, and so passes into solution:



The gold is recovered from the solution by passing it through a series of boxes containing zinc turnings, or by precipitation by zinc dust in deaerated cyanide solution.



The excess of zinc is removed by dilute acid, when the gold is left as a slime which is collected into a compact mass by fusion. This process enables quartz containing only three pennyweights of gold per ton to be worked profitably and under favourable conditions an even smaller quantity than this has been successfully extracted.

### Gold Refining

Crude gold often contains silver and copper. It is then usually purified by **parting with sulphuric acid**. If the alloy contains more than 30 per cent of gold it is not attacked by acid, and silver is added until the proportion is brought below this amount so as to render it susceptible to attack. The alloy is then boiled with concentrated sulphuric acid, when the silver and copper react with the acid, and the gold remains behind as a porous brown mass. This is washed, dried and fused into a compact mass.

**Electrolysis** is sometimes used. The alloy to be purified is made the anode, the cathode is pure gold, and the electrolyte a solution of gold chloride in hydrochloric acid. On electrolysis, gold is deposited on the cathode, while the silver forms a deposit of silver chloride near the anode.

**Parting by chlorine** is sometimes employed. The alloy is melted and chlorine is forced through it. Silver is converted to silver chloride which floats on the surface, other metals are volatilized off as chlorides, but the gold is unaffected.

Cupellation (as described under silver) can be used for removing base metals: the silver and gold remain and must be separated by parting with sulphuric acid or chlorine.

### § 26 Properties of Gold

Gold is a bright yellow metal when seen in the mass by reflected light; very thin sheets appear green or blue by transmitted light. Gold is one of the most malleable and ductile of metals, and its density, 19.3, is higher than that of all metals except rhenium, platinum, iridium and osmium.

Gold melts at 1063°; and the molten metal appears green. It begins to volatilize at temperatures just below its melting point and boils at 2660°. Gold occludes oxygen, hydrogen, and carbon monoxide under

suitable conditions. Gold is not acted upon by air or oxygen at any temperature, hence the alchemists called gold a *noble metal* in contrast with *base metals*—like copper, lead, tin, etc.—which are oxidized and lose their metallic character when heated in air. Silver and platinum are also noble metals.

Gold is scarcely affected by nitric, sulphuric, and hydrochloric acids, but it is attacked by aqua regia—i.e., a mixture of nitric and hydrochloric acid—or by a mixture of hydrochloric acid with an oxidizing agent which liberates chlorine; by water containing the halogens chlorine, bromine, or iodine in solution; and by solutions which can generate the halogens.

Gold is attacked by boiling ferric chloride solutions, hot selenic acid, telluric acid with sulphuric or phosphoric acid, alkaline sulphides and thiosulphates, perchlorates, perbromides, and periodides of the metals, iodic and periodic acids with hot sulphuric acid, and by reaction with substances which give large quantities of oxygen—manganese dioxide or potassium permanganate or nitric acid with sulphuric acid—and aqueous solutions of potassium cyanide when exposed to the air. Gold is not appreciably attacked by solutions of the alkalis. The freezing point of a solution of gold in mercury corresponds with a monatomic molecule Au.

### Colloidal Gold

Colloidal solutions of gold can be made by several methods and are stable for long periods. They can be obtained, for example, by Bredig's method (page 279) or by reduction of very pure, very dilute solutions of gold chloride, by means of such reagents as Rochelle salt (potassium sodium tartrate), formaldehyde, etc. Gold is thus formed in very minute particles, and the solution which is blue at first gradually becomes red.

The metallic gold can be removed from its colloidal solution by shaking the solution with precipitated aluminium hydroxide, stannic hydroxide, or barium sulphate. The decolorization here resembles the decolorization of coloured solutions by shaking them with recently ignited charcoal. The gold is adsorbed by the precipitating agent. Animal charcoal, if shaken with the solution, adsorbs the gold. The addition of electrolytes—acids, neutral salts, and alkalis—changes the red colour to blue, then violet, and then black. This is owing to the coagulation of the particles of gold into clots. The gold then settles to the bottom of the fluid. This behaviour is characteristic of colloidal solutions, as discussed in Chapter 19.

A form of colloidal gold known as **Purple of Cassius** has long been in use for colouring glass and enamels. It is made by mixing a solution of stannous and stannic chlorides with a very dilute solution of gold chloride. The gold is precipitated along with colloidal stannic acid, the result being a solid solution of the gold in the latter. In this way, the gold particles are "protected" and so the colour is remarkably stable.

### § 27 Uses of Gold

Gold has for long been the standard for the world's currency, and although it is no longer used for ordinary coinage purposes, it is still the final reserve of wealth and is held as such by all the principal Central Banks of the world in large amounts.

British gold coinage contained 91½ per cent of gold and 8½ per cent of copper. The Australian sovereign contained the same quantity of gold, but was alloyed with silver. Its colour was therefore a much less rich yellow than the British sovereign. American gold coinage was 90 per cent gold and 10 per cent copper.

Apart from its use as a standard of currency, and a reserve of wealth, the principal use of gold is in jewellery. For this purpose, as with coinage, the pure metal is too soft and it is, therefore, alloyed with other metals—usually copper. The fineness of a gold alloy is usually expressed in “carats.” Pure gold is “24-carat gold”; the sovereign was 22 carat since it contained 22 parts of gold to 2 parts other metal. Similarly, the other standard gold alloys recognized by law in England are 18-, 15-, 12- and 9-carat gold.

Gold also is used in considerable quantities in the form of *gold leaf* (obtained by beating gold down to a thickness of less than 0.00002 cm.) for signwriting, the lettering on the binding of books and for similar purposes. The so-called *liquid gold* (a suspension of very finely divided gold particles in vegetable oil) is used in the decoration of china articles.

Gold salts are used for toning in photography, and the use of “Purple of Cassius” in colouring glass has been mentioned above.

### § 28 Atomic Weight of Gold

The atomic weight of gold is seen to be in the neighbourhood of 200 from a consideration of its specific heat (0.0316), its position in the Periodic System and the molecular weight of compounds of gold in solution.

The combining weight has been found accurately by conversion of auric chloride into silver chloride, and by determination of the weight of gold remaining when potassium bromoaurate  $\text{KAuBr}_4$  is decomposed by heat. Electrolytic methods have also been used.

The value adopted at present by the International Committee (1957) is 197.0.

### § 29 Compounds of Gold

Gold forms two series of compounds, the aurous and auric, in which it is respectively univalent and trivalent. Since the electronic configuration of the gold atom is 2 8.18.32.18.1, two of the electrons of the penultimate shell must be used for the formation of the auric compounds. In this respect gold resembles copper and silver except that with them only one electron from the penultimate shell can be used for valency purposes. Gold has an extremely small atomic volume in relation to its high atomic number, which accounts for the fact that the auric compounds are almost certainly covalent and the aurous compounds are probably covalent also. The only definitely electrovalent compounds of gold are those containing it as the central atom of a complex ion, e.g., hydrochloroauric acid,  $\text{H[AuCl}_4\text{]}$ . In the aurous state the compounds are unstable and very readily disproportionate into auric compounds and metallic gold.

### § 30 Oxides and Hydroxides of Gold

Two oxides of gold have been described, viz.:

Aurous oxide,  $\text{Au}_2\text{O}$

Auric oxide,  $\text{Au}_2\text{O}_3$ .

The corresponding hydroxides are also known. All these compounds readily decompose on heating, leaving metallic gold.

**Aurous oxide**,  $\text{Au}_2\text{O}$ , is formed by precipitating a cold solution of gold in aqua regia with potassium bicarbonate. The brown flocculent precipitate is filtered off, washed, dried at  $110^\circ$  and washed with cold nitric acid to remove the more soluble auric oxide. The residue, after further washing and drying, consists of aurous oxide, possibly contaminated with a little metallic gold.

**Auric oxide**,  $\text{Au}_2\text{O}_3$ , is obtained by addition of potassium hydroxide solution to a boiling solution of auric chloride. It is a brown amorphous powder.

**Aurous hydroxide**,  $\text{AuOH}$ , is said to be formed as a violet powder when a dilute solution of potassium hydroxide is added to cold aurous chloride or bromide solution.

**Auric hydroxide**,  $\text{Au}(\text{OH})_3$ , is obtained as an orange-coloured precipitate when cold solutions of potassium hydroxide and auric chloride are mixed. It loses water at  $100^\circ$ , forming  $\text{AuO} \cdot \text{OH}$ ; further heating forms auric oxide, and finally metallic gold. Auric hydroxide is soluble in excess of alkali, forming potassium aurate,  $\text{KAuO}_2$ , which is precipitated on addition of nitric acid. It is a crystalline salt, soluble in water. Several other aurates are known, and auric hydroxide, though amphoteric, more readily behaves as an acid, and hence is sometimes called **auric acid**.

### § 31 Other Compounds of Gold

Both oxides mentioned above give rise to salts, all of which are unstable and readily decomposed, leaving the metal behind.

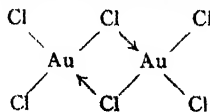
**Aurous chloride**,  $\text{AuCl}$ , is made by heating auric chloride, freed from traces of hydrochloric acid, to a temperature between  $170^\circ$  and  $180^\circ$ . Any unchanged auric chloride is removed by washing with thoroughly dried ether. In contact with water it decomposes, forming auric chloride and gold: with hydrochloric acid aurous oxide reacts similarly:



When heated above  $180^\circ$ , it reverts to the metal and when treated with dry chlorine passes into auric chloride.

**Auric chloride**,  $\text{AuCl}_3$ . If gold be dissolved in a mixture of concentrated hydrochloric and nitric acids (aqua regia) yellow needle-like crystals of **chloroauric acid**,  $\text{HAuCl}_4$ , separate on concentrating the solution. When heated in a current of chlorine at  $200^\circ$ , auric chloride (mixed with a little gold and aurous chloride) is formed in dark red crystals. Auric chloride is readily decomposed on heating, forming first aurous chloride and then metallic gold. The *gold chloride* of commerce is chloroauric acid, which is much more stable, and is used in photography. A series of complex salts called the chloroaurates is known, e.g.,  $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$ , etc.

The vapour density of auric chloride shows that it has the molecular formula  $\text{Au}_2\text{Cl}_6$ ; it probably should be represented as having the structure



### § 32 Detection and Determination of Gold

A very sensitive test for the detection of gold in solution is by the addition of a dilute solution of stannous and stannic chlorides, when the formation (rapidly on warming) of "Purple of Cassius" is evidence of the presence of gold.

It is usually determined by *assaying*, which consists in heating a known weight of the gold-containing substance (e.g., an ore) with lead oxide, charcoal and soda-ash (anhydrous sodium carbonate) in a crucible. There is thus formed a bead of metallic lead containing any gold and silver present. This bead is removed and heated on a small cupel (page 665) until the lead has been oxidized. The silver-gold bead remaining is heated with nitric acid to remove the silver, after which the residue of gold is heated to redness, cooled and weighed.

### § 33 Relationships of the Elements of Group I

The older forms of the Periodic Table, such as that on page 125, placed all the elements considered in this chapter and Chapter 28 in one group in such a way as to emphasize (or even overemphasize) the relationship between the two sub-groups. The later form of the table given on page 127, while preserving the connection between the sub-groups, indicates clearly that copper, silver and gold are **transition** elements, and hence that resemblances to neighbouring elements in the same period (i.e., what are sometimes called horizontal relationships) are to be expected.

The alkali metals themselves (viz., lithium, sodium, potassium, rubidium and caesium) form a very satisfactory "family" of elements, showing an appropriate gradation of properties in passing from one to another. The gradation in physical properties is illustrated by Table XLI.

TABLE XLI.—PHYSICAL PROPERTIES OF THE ALKALI METALS

	Lithium	Sodium	Potassium	Rubidium	Caesium
Atomic number . . .	3	11	19	37	55
Atomic weight . . .	6.94	22.991	39.100	85.48	132.91
Specific gravity . . .	0.53	0.97	0.859	1.53	1.9
Atomic volume . . .	13.1	23.7	44.4	55.8	69.3
Melting point . . .	186.0°	97.7°	63°	38.8°	29.7°
Boiling point . . .	1380°	883°	760°	679°	690°
Specific heat at 0° . .	0.941	0.2811	0.1728	0.0802	0.0522
Coefficient expansion .	0.000153	0.000274	0.000282	0.000338	0.000345
Heat of fusion (Cals.) .	32.81	27.21	14.67	6.144	3.766
Increased volume on fusion (per cent) . .	1.51	2.03	2.44	—	—
Heat of conversion R <sub>2</sub> O to R <sub>2</sub> O <sub>3</sub> (Cals.)	7.91	19.03	22.0	24.1	25.0
Lowest temp. of reaction with water .	—	-98°	-105°	-108°	-116°

In the case of the elements of the B sub-group, viz., copper, silver and gold, the relationship is less close than among the alkali metals, and, furthermore, marked resemblances are found to the neighbouring

transition elements. The relationship between the alkali metals on the one hand, and copper, silver and gold on the other, is very slight.

The principal physical properties of copper, silver and gold are given in Table XLII.

TABLE XLII.—PHYSICAL PROPERTIES OF COPPER, SILVER, AND GOLD

	Copper	Silver	Gold
Atomic number . . . .	29	47	79
Atomic weight . . . .	63.54	107.88	197.0
Specific gravity . . . .	8.9	10.5	19.3
Atomic volume . . . .	7.14	10.27	10.2
Melting point . . . .	1083°	960.8°	1063°
Boiling point . . . .	2582°	2193°	2660°
Latent heat of fusion (Cals) .	43	24.35	16.08
Specific heat . . . .	0.09	0.055	0.030

The alkali metals also are all silvery white, soft enough to be cut with a knife, of very low density and characterized by remarkably intense chemical activity. Their chemistry accords satisfactorily with that which would be inferred from the accepted structures of their atoms and present theories of valency (cf. Chapter 11). Thus, as in Table XII, the electronic configurations of these elements are:

Li	2.1		
Na	2.8.1	Cu	2.8.18.1
K	2.8.8.1	Ag	2.8.18.18.1
Rb	2.8.18.8.1	Au	2.8.18.32.18.1
Cs	2.8.18.18.8.1		

The alkali metals have a single electron in the outermost shells which, when removed, leave positive ions with the very stable Inert Gas structure. Their large atomic volumes indicate that they have a large electronic radius; the outermost electron is, therefore, a considerable distance from the nucleus and so is easily removed. This effect becomes greater with increasing Atomic Number since the distance of the outermost electron is greater and so is the screening effect of the remaining extra-nuclear electrons. Consequently, these elements are strongly electropositive, form cations very readily and their chemical activity and electropositive character increase in passing from lithium to caesium, which is the most electropositive of all the commoner elements known. Element No. 87, francium, when it has been sufficiently investigated will, no doubt, be found to be even more electropositive than caesium.

The readiness with which the outermost electron of an alkali metal is lost is matched by the reluctance of the ion so formed to take up an electron and re-form the metal. In order to force the ion to acquire an electron it is necessary to use either electrolysis or a very powerful reducing agent. The metals are therefore very reactive and do not



form covalent or co-ordinate bonds. Again lithium carbonate (like the carbonates of the alkaline earths) decomposes on heating but the carbonates of the other alkali metals do not. This is because the lithium ion, having a small radius, has a greater, though still slight tendency to attract electrons and so distorts the carbonate ion sufficiently to cause it to decompose on heating; in the larger ions (sodium to caesium) this tendency is too small for decomposition to occur.

The salts of the alkali metals are nearly all soluble in water, and are the most stable of all metallic salts. Their physical properties show the same order of variation as the atomic weights of the elements. Lithium differs in some respects from the others, an example of the fact that the first member of a family (i.e., the elements of the first short period) often exhibit such differences (cf. beryllium, boron, fluorine). Thus, lithium carbonate, phosphate, and fluoride are very much less soluble than the corresponding salts of the other members. And in this respect, lithium resembles the members of the calcium family, and it thus forms a connecting or bridge element between the alkalis and alkaline earths. The alkali sulphates form isomorphous characteristic alums (q.v.), but lithium alum crystallizes only below 0° C. and sodium alum is very soluble and difficult to prepare. Lithium carbonate is sparingly soluble in water, sodium carbonate is not deliquescent, the others are. The salts of sodium and lithium form stable hydrates with water, whereas potassium, rubidium, and caesium salts are nearly all anhydrous. But sodium resembles lithium in the solubility of its chloroplatinate, acid tartrate, and alum, so much so that the alkali metals are sometimes divided into two classes: (1) those with sparingly soluble chloroplatinates—viz., potassium, rubidium, and caesium; and (2) those with soluble chloroplatinates—viz., lithium and sodium.

By contrast with the alkali metals the loss of the outermost electron from the atoms of copper, silver or gold leaves not an inert gas structure, but the less stable group of eighteen electrons. The comparative instability of the eighteen group is indicated by the fact that nickel, palladium and platinum, which immediately precede copper, silver and gold in their respective periods, are not inert gases but metals (i.e., they readily lose electrons to form metallic ions). The result of this is seen in the variable valency exhibited by copper and gold (and to a much smaller extent by silver) owing to the possibility of the removal of one or more of the electrons from the 18-electron shell.

The metals copper, silver and gold hence differ markedly from the alkali metals in almost every respect except in their univalent compounds, and even here the smaller stability of the 18- as compared with 8-electron shell very considerably modifies the resemblance.

On the other hand, these three metals come close to the end of the series of transition elements in their several periods, i.e., the process of expanding the penultimate shell of electrons from 8 to 18 is just complete. Hence considerable resemblances between them and their "horizontal" neighbours are to be expected, e.g., between nickel,

copper and zinc; palladium, silver and cadmium; and between platinum, gold and mercury. Such resemblances are, in fact, very marked, e.g., divalent copper closely resembles nickel and zinc; platinum has many properties similar to gold, and but few to nickel.

In malleability, ductility, and tenacity, silver is intermediate between copper and gold. It is noteworthy that copper and gold are the only metals known which do not show a *white* lustre. While the large atomic volume of the alkali metals is associated with the great chemical activity and affinity for oxygen, the low atomic volume of these elements is related to their weak affinity for oxygen, etc. Copper, for instance, is alone oxidized in air. The oxides of copper, silver, and gold are easily reduced, while the oxides of the alkali metals are reduced with great difficulty. The reduction of copper, silver, and gold by magnesium is the more energetic the greater the atomic weight of the metal—cuprous oxide is easily reduced; silver oxide is reduced with explosive violence, and gold oxide breaks down into its constituents below the ignition point of magnesium. Copper and silver are both uni- and bivalent, and gold is uni- and trivalent. Hence these three elements have univalency in common with the alkali metals. Cupric salts are isomorphous with iron, cobalt, and nickel salts. The more salient differences between copper, silver and gold and the alkali metals are: (1) the elements of the alkali metals have a small density, the other metals have a large density; (2) the alkali metals do not occur free; (3) the elements of the alkali metals are chemically active, the others not so; (4) the haloids of the alkali metals are all soluble in water, and are not hydrolysed by water; copper and silver form sparingly soluble haloids, and the haloids of copper and gold, not silver, are hydrolysed by water; (5) the oxides and hydroxides of the alkali metals are strongly basic; the oxides and hydroxides of copper and gold are feebly basic, and they accordingly form basic salts; (6) the alkali metals do not form complex salts, whereas copper, silver, and gold form many complex salts.

The remarkable difference between the cuprous and cupric salts—whereby the former make copper resemble silver, and the latter relate it to zinc, ferrous iron, and nickel—emphasizes very forcibly the fact that the properties of an element which forms compounds of a particular valency bear no necessary relation with the properties of the same element which forms compounds with a different valency.

Many resemblances are discernible also between silver and mercury. The halides are remarkably similar. The two chlorides are white, the bromides distinctly yellow, and the iodides yellow. The yellow mercurous halides are more intensely coloured than the corresponding silver halides. The same remark applies to the nitrites and hyponitrites. *Monad* mercury is closely related to *monad* silver, far more closely than gold to silver.

## CHAPTER 30

# THE ALKALINE EARTH METALS

### § 1 Group II of the Periodic Table

THE elements of the second group are: beryllium, magnesium, calcium, strontium, barium and radium in the A sub-group, with zinc, cadmium and mercury in the B sub-group. The relationship between the two sub-groups is much more marked than in Group I, so that opinions differ as to whether magnesium should be particularly associated with calcium, etc., or with zinc, etc. Good reasons can be adduced for either arrangement since magnesium exhibits marked resemblances both to calcium and to zinc.

The relationships between these elements and the gradations of properties are discussed at the end of Chapter 31.

### § 2 Beryllium

#### History

While analysing beryl, in 1797, L. N. Vauquelin found that a precipitate which he thought to be aluminium hydroxide, dissolved like aluminium hydroxide in potassium hydroxide; but unlike aluminium hydroxide, the solution furnished a white precipitate when boiled for some time. Unlike aluminium hydroxide, too, the precipitate was soluble in ammonium carbonate, and behaved in many other ways differently from aluminium hydroxide. Hence L. N. Vauquelin announced the discovery of a new earth—"la terre du Beril," in 1798.

At the time the name glucina—from the Greek *γλυκος* (*glucus*), sweet—was suggested for this "earth" since some of its salts have a sweet taste; but the term *beryllia* (and hence beryllium for the element itself) is now used almost exclusively. The metal was first isolated by Wöhler in 1828 by the action of potassium on beryllium chloride.

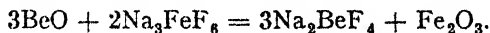
#### Occurrence and Extraction

The mineral *beryl*,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , is the principal source of beryllium. The beryls include the gem-stones *emerald* and *aquamarine*. Recently a new low-grade ore of magnetite containing small quantities of *helvite* (a beryllium iron aluminium silicate) is said to have been worked successfully (see below). Although there are minerals richer in this element, they are scarce and costly. Beryllium is not very abundantly distributed in nature, but small quantities are found in a great many minerals.

The production of beryllium compounds from beryl is made difficult by the comparative resistance of beryl, the only ore available in quantity, to attack by reagents and by the rather difficult separation from aluminium. The simplest method is to fuse the ore in an electric furnace at  $1500^{\circ}$ – $1600^{\circ}$  and quench the product in cold water. The resulting vitreous mass is crushed and now reacts readily with concentrated sulphuric acid. This produces partially hydrated sulphates of aluminium and beryllium which are leached out from the accompanying silica by means of water. Excess of ammonium sulphate is added which causes precipitation of ammonia alum which is very sparingly soluble in beryllium sulphate solution containing excess of ammonium sulphate. Any ferrous oxide present is oxidized by means of hydrogen peroxide and precipitated by addition of calcium carbonate. After filtration beryllium hydroxide is precipitated by means of ammonia.

An alternative method now being used consists in sintering beryl at  $800^{\circ}$  with sodium hydrogen fluoride which converts the beryllium present into a sodium beryllium fluoride (possibly  $\text{Na}_2\text{BeF}_4$ ) which can be extracted with water from the residue of silica and alumina. From this beryllia is precipitated by alkali.

A recently described process uses sodium ferric fluoride,  $\text{Na}_3\text{FeF}_6$ , as the attacking reagent which similarly reacts preferentially with the beryllium of the ore, leaving alumina, silica and iron oxide (if present) unattacked:



This process is said to make possible the use of the new low-grade ore containing helvite, referred to above.

The metal is obtained by electrolysis of a fused mixture of beryllium and potassium chlorides at  $350^{\circ}$  and also by the reduction of beryllium fluoride by metallic magnesium.

For use in nuclear reactors very pure beryllium (or beryllium oxide) is required. Purification can be achieved by distillation under reduced pressure and also by distillation of the basic acetate from which beryllium oxide can be recovered by heating to  $700^{\circ}$ .

The necessary anhydrous beryllium chloride for the former process is now made by chlorinating briquettes of beryllium oxide and carbon at  $700^{\circ}$ – $800^{\circ}$ . The chloride sublimes and is further purified by fractional sublimation in a current of hydrogen.

Alloys of beryllium (e.g., with copper or nickel) can be obtained by reduction of the oxide with carbon in presence of the alloying metal.

### Properties

Beryllium is a hard, silver-white metal of low density (1.8) and high melting point ( $1300^{\circ}$ ). In chemical properties it is similar in some respects to magnesium; but it does not react with water, even at a red heat; while it resembles zinc and aluminium in its reaction with caustic alkali solutions. Its oxide is only feebly basic, its chloride is volatile

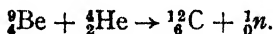
and fumes in air, like aluminium chloride, and in many respects it closely resembles aluminium. The resemblance of lithium to calcium was mentioned in Chapter 29 (page 681): the similarity between beryllium and aluminium is even more marked.

### Uses

Until quite recently beryllium was a chemical curiosity; but it is now beginning to be made for use in alloys: in particular in the form of beryllium bronzes by alloying with copper. A typical alloy may contain 2.25–2.5 per cent of beryllium.

These beryllium bronzes are characterized by great hardness and tensile strength. With suitable heat treatment they acquire the strength and hardness of spring steel and their resistance to fatigue and corrosion and their good electrical conductivity and non-sparking properties make them of value for contacts, brush-holder springs, slip-rings for high-speed motors, valve-springs, etc. The alloys of beryllium with aluminium, nickel and cobalt are also being investigated with a view to application in aircraft construction, etc. All these alloys exhibit marked resistance to corrosion. Beryllium itself is now being used for the "windows" of X-ray tubes since it is seventeen times more transparent to X-rays than corresponding amounts of aluminium.

Beryllium is important as a source of neutrons which are formed when it is bombarded with  $\alpha$ -particles:



Beryllium is also employed to reduce the velocity of neutrons since the small mass of the nucleus makes it possible for it to do this with very little loss of energy. Beryllium zinc silicate is used in the "coating" of some forms of fluorescent lamp. Beryllium compounds are poisonous and care is therefore necessary when handling them. This applies also to the coatings of fluorescent lamps when broken.

Beryllium possesses a number of properties, notably its high melting point, resistance to oxidation in carbon dioxide (both wet and dry) and high-temperature strength which recommend it for use as a possible fuel-canning material for gas-cooled nuclear reactors, and much work is being done on this subject.

The **atomic weight** of beryllium was for a time uncertain. Its combining weight is in the neighbourhood of 4.5, and for a considerable period, owing to its resemblance to aluminium, it was assumed to be trivalent and to have an atomic weight approximating to 13.5. Dulong and Petit's rule indicates a value about 15, at ordinary temperatures, but this value rapidly falls at higher temperatures to about 10. The periodic classification, however, has no place for a trivalent element of atomic weight 13.5, but has a place for a bivalent one of 9 approximately. Accordingly, it was proposed to put beryllium into this vacant space on

the assumption that it is a bivalent element. This was confirmed by the determination of the vapour density of the chloride which is approximately 40 ( $H_2 = 1$ ). The most recent accurate determinations of the combining weight, made by Hönigschmid by converting pure beryllium chloride into silver chloride, led to the value 9.018 for the atomic weight and 9.013 is the value approved by the International Committee at the present time.

### Compounds of Beryllium

**Beryllium oxide**,  $BeO$ , can be obtained by igniting the metal, nitrate, etc., in air, but is usually made from beryl. It is a white, insoluble powder, which forms beryllium salts with acids, and also reacts with caustic alkali solutions, forming, e.g.,  $K_2BeO_2$ .

The salts resemble those of magnesium in properties, but they also resemble those of aluminium, e.g., in the volatility and the easy hydrolysis of the chloride. Beryllium also readily forms basic salts.

Beryllium is notable for the readiness with which it forms complex compounds, particularly with organic compounds. One of the best known of these is the so-called **basic beryllium acetate** which is made by the addition of beryllium hydroxide to acetic acid. Its composition is represented by the formula  $Be_4O(CH_3COO)_6$ . It is a covalent compound and not a salt as is indicated, *inter alia*, by its low boiling point ( $330^\circ$ ) and melting point and by the possibility of distilling it without decomposition.

### § 3 Magnesium, Mg. History and Occurrence

In 1695 N. Grew published a pamphlet describing a peculiar salt found in the mineral springs at Epsom. The medicinal properties of this salt attracted some attention; in England the salt was called "Epsom salt," and on the Continent, "sal anglicum." *Magnesia alba* (a basic magnesium carbonate) came into commerce from Rome about 1700; the term "*magnesia alba*" was applied to the earth owing to some fanciful contrast with "*magnesia nigra*," the term then used for black oxide of manganese. In 1755 J. Black clearly distinguished between *magnesia* and lime by showing that *magnesia* furnished a soluble sulphate, and lime a sparingly soluble sulphate. When H. Davy isolated the impure metal in 1808, he called it "magnium." At that time the terms "magnesium" and "manganese" were applied synonymously to the element (manganese) derived from the mineral pyrolusite (manganese dioxide). To avoid confusion, the term "magnesium" was soon afterwards restricted to the element derived from *magnesia alba*; and "manganese" to the element derived from pyrolusite.\*

\* It is not very clear whether the term "*magnesia*" is a corruption of the word *Mangana* in the East Indies, or whether "*manganese*" is a corrupted form of the word *Magnesia*, a locality in Asia Minor.

Magnesium occurs in nature combined, not free, as magnesium carbonate in *magnesite*,  $\text{MgCO}_3$ ; double carbonate of calcium and magnesium in *dolomite*,  $\text{MgCO}_3 \cdot \text{CaCO}_3$  or  $(\text{Mg}, \text{Ca})\text{CO}_3$ ; magnesium sulphate in *Epsom salts*,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ; and *kieserite*,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ; magnesium chloride in *carnallite*,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and *kainite*,  $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; magnesium silicate in *olivine*,  $\text{Mg}_2\text{SiO}_4$ ; *enstatite*,  $\text{MgSiO}_3$ , etc. Magnesium is also common in many other minerals; e.g., asbestos, steatite, spinel, meerschaum, serpentine, talc, etc.

Magnesium compounds also occur (to the extent of about 0.13 per cent) in sea-water, which is now being used as a commercial source of magnesia refractories and of magnesium metal.

#### § 4 Manufacture of Magnesium

Magnesium is now manufactured on a large scale by the electrolysis of fused mixtures of magnesium chloride and other chlorides and by the thermal reduction of calcined dolomite,  $\text{MgO} \cdot \text{CaO}$ , with silicon.

Anhydrous magnesium chloride for electrolysis in the type of cell illustrated in Fig. 30 1 is produced by passing chlorine at red heat over

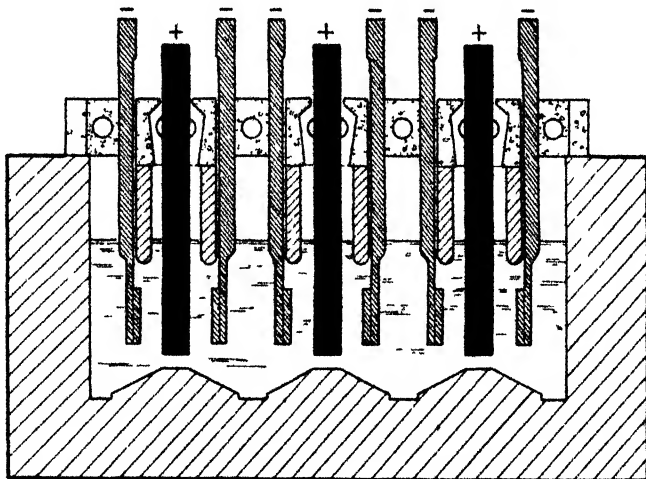
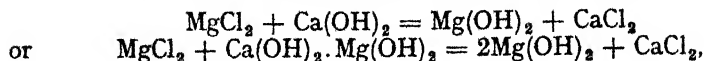


FIG 30 1 —Manufacture of Magnesium from  
Anhydrous Magnesium Chloride

a mixture of carbon and sea-water magnesia or calcined magnesite. In theory, all the chlorine needed for this chlorination process should be obtainable from the subsequent electrolysis of the magnesium chloride, but, in practice, there is a loss which must be made up by introducing some fresh chlorine. The sea-water magnesia is obtained

by treating filtered sea-water with a slight excess of slaked lime,  $\text{Ca(OH)}_2$ , or slaked calcined dolomite,  $\text{Ca(OH)}_2 \cdot \text{Mg(OH)}_2$ . Magnesium hydroxide which is precipitated according to the reactions,



is filtered off and calcined.

The cell of Fig. 30.1, which was first developed in Germany and then introduced in other countries, consists of a rectangular steel tank lined with heat-insulating and refractory brickwork. The compact parallel electrode arrangement of two cast steel cathodes on either side of a flat graphite anode assembly provides a large electrode surface and thus a high current load per unit volume of cell. Refractory, electrically non-conducting, curtain plates separate the anode and cathode compartments and prevent recombination of the floating magnesium metal which collects at the cathode with the chlorine which is evolved at the anode, and bubbles upwards through the electrolyte into the chlorine collecting system.

In the Dow electrolytic process, currently used in U.S.A., magnesium chloride solution, obtained by dissolving sea-water magnesium hydroxide in hydrochloric acid, is spray-dried to a solid hydrated magnesium chloride of the approximate composition  $\text{MgCl}_2 \cdot 1.25\text{H}_2\text{O}$ . Because the "cell feed" is hydrated, the anode products of the Dow cell are chlorine, hydrogen chloride and carbon dioxide. The chlorine in these gases is converted into hydrogen chloride by heating to at least  $1000^\circ \text{C}$ . with several times its volume of water vapour in a furnace fired by gas or oil. The hydrochloric acid produced by absorbing the hydrogen chloride in water is used for neutralization of the magnesium hydroxide. The design of the Dow cell differs from that of the cell of Fig. 30.1. The anodes are adjustable to allow for loss of carbon by oxidation to carbon dioxide.

Magnesium chloride is a minor constituent by weight of the fused mixtures which are electrolysed to molten magnesium metal. The greater part of the electrolyte consists of sodium, potassium, calcium or barium chlorides in proportions chosen so as to confer greater density, greater electrical conductivity, lower melting point, and other desirable physical properties to the electrolyte. However, magnesium is the only metal liberated from the fused mixture because the decomposition voltage of magnesium chloride at the operating cell temperature is much lower than that of the other chlorides.

The reducing agent used in the thermal reduction of calcined dolomite by silicon is 75 per cent ferrosilicon obtained from silica, coke and steel scrap in electric furnaces. In the Pidgeon process developed in Canada, a mixture of finely calcined dolomite and 75 per cent ferrosilicon, pressed into small briquettes, is heated to about  $1150^\circ \text{C}$ . under high vacuum, in electrically heated heat-resisting steel retorts. The magnesium vapour produced under these conditions is condensed to a



solid "crown" of shiny magnesium crystals. Processes based on the same reaction but using different reduction furnaces and other methods of heating have been introduced, first in Germany, and later in France, U.K., Italy and U.S.A., but the Pidgeon process was the first to be operated successfully on a large industrial scale.

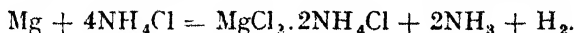
Shortly before and during the Second World War it was hoped that the electrothermic reduction of magnesia by carbon could be carried out industrially. Reduction by carbon to magnesium vapour and carbon monoxide takes place at  $2200^{\circ}\text{C}$ ., but the reaction is reversed at lower temperatures so that instantaneous quenching is necessary. The use of hydrogen and hydrocarbon vapour for this purpose has been extensively investigated, but the process has remained dangerous and difficult and it is unlikely that it will ever be successful.

### § 5 Properties of Magnesium

Magnesium is a silvery-white metal of low specific gravity (1.74). It melts at  $650^{\circ}$  and boils at  $1100^{\circ}$ . It is not affected by dry air at ordinary temperatures; but when heated, burns in air giving a brilliant white light of great actinic power and forms a mixture of magnesium oxide and nitride. It reacts readily with most non-metals, e.g., the halogens, sulphur, phosphorus, etc., and nitrogen with which it easily forms a nitride  $\text{Mg}_3\text{N}_2$ . Magnesium reacts very slowly with water at ordinary temperatures, and rather less slowly at  $100^{\circ}$ ; but when heated in a current of steam, it takes fire and continues burning:



Magnesium reacts readily with dilute mineral acids with liberation of hydrogen, being the only metal besides manganese which will liberate this gas from dilute nitric acid. (The conditions must, however, be very carefully controlled and the acid very dilute; about 1 per cent: more concentrated acid gives oxides of nitrogen.) Concentrated sulphuric acid attacks magnesium when hot, liberating sulphur dioxide. Solutions of the alkalis do not attack magnesium, which, since it is a strongly electropositive metal, will displace almost all metals from their salts. (Cf. Table XIX, page 231.) It also reacts with aqueous solutions of ammonium salts with evolution of hydrogen. With ammonium chloride it has been stated that a double salt is formed:



Magnesium reduces most oxides, and will burn in carbon dioxide, sulphur dioxide, and nitric oxide, for example. It will also reduce sodium and potassium oxides on heating.

### § 6 Uses of Magnesium

Magnesium in the form of ribbon is familiar in laboratories; likewise the brilliant light with which it burns.

Many metals, for example iron, burn very readily in air when in the form of powder or very thin sheet, but are extremely stable to oxidation at ordinary temperatures when massive. Magnesium is similar, and on account of its low density, the good mechanical and other physical properties, and the machinability of its alloys, it is being increasingly used as a structural metal, particularly where weight-saving is important. The aircraft industry makes extensive use of magnesium alloys.

Aluminium and manganese are valuable alloying metals. Magnesium-rich alloys containing zirconium with zinc and rare earths or thorium, have been discovered in the last ten years or so, particularly in the U.K.

Magnesium is "transparent" to thermal neutrons, and in the form of "Magnox" alloy, resistant to the action of carbon dioxide at about 350° C., is the metal in which the uranium fuel elements of present-day gas-cooled nuclear power reactors are enclosed. Much magnesium metal is used nowadays in the form of protective anodes, to inhibit corrosion of steel and iron in ships and underground pipe lines.

Magnesium is introduced into aluminium to produce very useful high-strength aluminium-rich alloys.

The metal is being increasingly used in industry as a chemical reagent, for example in the reduction of uranium fluoride to uranium metal and in the production of synthetic organic chemicals.

### § 7 Atomic Weight of Magnesium

A value in the neighbourhood of 24 is indicated for the atomic weight of magnesium by the Periodic Table, and the specific heat of metallic magnesium. The best determinations have utilized the conversion of magnesium chloride into silver chloride, or the conversion of the pure oxide into the sulphate. Richards, using the former method, obtained results leading to values very close to 24.32, which is the number at present recommended by the International Committee.

### § 8 Magnesium Hydride, Oxide and Hydroxide

**Magnesium hydride**,  $\text{MgH}_2$ , has been obtained by the action of lithium aluminium hydride on dimethyl magnesium in ether and also by heating diethyl magnesium to 175° in a high vacuum. It is a colourless solid which reacts violently with water.

**Magnesium oxide**,  $\text{MgO}$ , can be obtained (mixed with a little nitride) by burning the metal in air, but commercially it is made by heating the carbonate:



or the hydroxide obtained from sea-water as described on page 688. Some is also recovered from the waste magnesium chloride of the potash industry (page 640) by means of slaked lime in the same way.

Magnesium oxide is a white powder, slightly soluble in water. Thus 100 grams of water dissolve about 0.0006 gram of magnesium oxide (or magnesia). The solution has a slightly alkaline reaction. It is curious that the higher the temperature used in calcination, the lower the solubility of the resulting magnesia. This has been ascribed to polymerization, but has not been definitely proved, and it may be that the *rate* of dissolution is lower. In the magnesite brick industry the favourite theory is that the material made at low temperatures is non-crystalline and that made at high temperatures is crystalline. It is a very refractory material, only fusing at  $2800^{\circ}$ , and so is used for lining basic steel and other metallurgical furnaces, for making refractory bricks, crucibles, etc. A paste of water and magnesia (calcined at low temperature) "sets" like mortar. It gradually rehydrates and absorbs carbon dioxide from the air and forms a hard mass.

Magnesia is a basic oxide and reacts readily with dilute acids. It is used in medicine for correcting acidity.

**Magnesium hydroxide**,  $\text{Mg}(\text{OH})_2$ , is precipitated from solutions of magnesium salts by addition of solutions of alkali hydroxides. It is *less* soluble than slaked lime (q.v.), hence it is possible to obtain it as above from magnesium chloride and slaked lime. It is soluble in solutions of ammonium salts and so is incompletely precipitated by ammonia, and if sufficient ammonium salt be present will not be precipitated at all (page 265).

Magnesium hydroxide is used in the sugar industry for the extraction of sugar from molasses. (Cf. similar use of strontium hydroxide, page 707.)

### § 9 Magnesium Salts

Magnesium hydroxide is a fairly strong base and forms well-defined salts with acids. They are colourless (except when formed from a coloured acid) and are not poisonous. Those with strong acids are usually soluble; the carbonate, phosphates and fluoride are sparingly soluble. Many of the salts crystallize with considerable amounts of water, e.g.,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ .

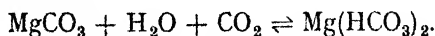
#### **Magnesium Carbonate, $\text{MgCO}_3$**

Magnesium carbonate occurs in enormous quantities associated with calcium carbonate as *dolomite*,  $\text{MgCO}_3 \cdot \text{CaCO}_3$ ; it is also found as *magnesite*,  $\text{MgCO}_3$ . The anhydrous carbonate can be prepared by preparing a solution of magnesium sulphate and sodium bicarbonate supersaturated with carbon dioxide and heating so that the gas can only escape slowly. A hydrated carbonate,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , slowly separates when solutions of magnesium sulphate and sodium bicarbonate are mixed and allowed to stand for several days when it is

slowly deposited as a white powder. If sodium carbonate solution is used instead, various *basic* carbonates result. If the precipitation be carried out in the cold with dilute solutions, the *magnesiï carbonas levis* (light magnesium carbonate) of pharmacy results. Hot concentrated solutions similarly yield *magnesiï carbonas ponderosa* (heavy magnesium carbonate). These have been said to have the compositions  $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  and  $3\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$  respectively, but it is very doubtful if either is a pure compound.

The various basic carbonates are extensively used in the salt, rubber and printing-ink industries, and also in pharmacy, etc., for the production of toothpastes, face-powders, etc.

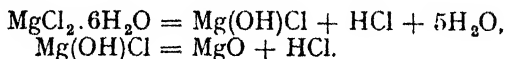
All these magnesium carbonates are insoluble in water, and on heating yield magnesium oxide. The normal carbonate is soluble in water saturated with carbon dioxide owing to the formation of **magnesium bicarbonate** :



Like most magnesium salts it is also soluble in solutions of ammonium salts. Magnesium bicarbonate usually occurs along with calcium bicarbonate in natural waters, contributing then to their temporary hardness (see page 308).

### Magnesium Chloride, $\text{MgCl}_2$

This salt occurs in sea-water, and is also found in quantity (e.g., at Stassfurt) as *carnallite*,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . It is thus a by-product of the potash industry, and is used as a source of magnesium oxide. Magnesium chloride can be prepared in the laboratory in the usual way, and crystallizes from solutions as  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . This cannot be dehydrated by heat since hydrogen chloride is lost as well as water leaving an oxychloride which, on heating to  $600^\circ$ , is converted into the oxide. It is not certain that the oxychloride is a single substance of definite composition but the changes are usually represented:



The anhydrous salt can be obtained by dehydration in a stream of hydrogen chloride. Magnesium chloride is hydrolysed slightly in water, and hence its presence in boiler feed water is very obnoxious. The crystallized salt is very deliquescent, and is used in cotton-spinning as a lubricant for the thread.

When a concentrated solution of magnesium chloride is made into a thick paste with calcined magnesia, the mixture hardens to a stone-like mass owing to the formation of an oxychloride. This mixture is used under the name of *Sorel's cement* for making artificial stones, floors, etc.

**Magnesium bromide**,  $\text{MgBr}_2$ , occurs in sea-water, and is used as a source of bromine (see page 557). **Magnesium iodide**,  $\text{MgI}_2$ , is also found in the sea.

**Magnesium nitrate**,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , crystallizes out of the solution formed by adding the oxide or carbonate to dilute nitric acid. It is deliquescent.

### **Magnesium Sulphate, $\text{MgSO}_4$**

Magnesium sulphate occurs as *kieserite*,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , in the Stassfurt deposits. When kieserite is digested with water, and the solution purified by recrystallization, colourless rhombic prisms of the heptahydrate— $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ —separate from the cold solution. When the temperature is about  $30^\circ$ , monoclinic prisms of the hexahydrate— $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ —are formed. Several hydrates are revealed when the solubility of magnesium sulphate is studied. At  $150^\circ$  the crystalline salt passes into the monohydrate, *kieserite*,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ; and at  $200^\circ$  the anhydrous salt is obtained with partial decomposition. Magnesium sulphate forms a series of double salts, e.g.,  $\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , *schonite*, crystallizing in monoclinic prisms, isomorphous with  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . Like barium sulphate, crystals of the acid salt  $\text{MgSO}_4 \cdot \text{H}_2\text{SO}_4$  are deposited from a hot solution of magnesium sulphate in sulphuric acid; and from cold solutions, the acid salt  $\text{MgSO}_4 \cdot 3\text{H}_2\text{SO}_4$  is crystallized. Crystalline magnesium sulphate— $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ —is also called "Epsom salts," or *epsomite*, because it occurs abundantly in the water of the Epsom springs. This salt is used in medicine; in the tanning and dyeing industries; and in the manufacture of paints and soaps.

Epsom salts are freely soluble in water: 100 grams of water will dissolve 71 grams of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  at  $20^\circ$ .

### **Magnesium Ammonium Phosphate, $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$**

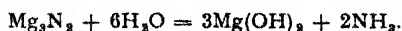
This salt is obtained as a crystalline precipitate when a solution of a soluble phosphate is mixed with ammonia, ammonium chloride and magnesium sulphate or chloride; and conversely, if ammonium phosphate be added to an ammoniacal solution of a magnesium salt the same substance is precipitated. When the precipitated magnesium ammonium phosphate is filtered, washed, dried and heated, it is converted into magnesium pyrosulphate:



This reaction is made use of in the determination both of magnesium and of phosphates.

### **Magnesium Nitride, $\text{Mg}_3\text{N}_2$**

When magnesium is heated in nitrogen, or in ammonia gas, magnesium nitride is formed. Hence a small quantity is formed, along with the oxide, when magnesium burns in air. This property of magnesium was made use of by Ramsay for the isolation of the Inert Gases (page 590). Magnesium nitride is a yellowish powder, which is decomposed by water into the hydroxide and ammonia:



### § 10 Detection and Determination of Magnesium

Magnesium is usually detected by the facts that:

(i) In presence of ammonium salts it is not precipitated as sulphide, hydroxide or carbonate; thus distinguishing it from all except the alkali metals; (ii) when mixed with ammonia, ammonium chloride and ammonium phosphate the double magnesium ammonium phosphate— $\text{Mg}(\text{NH}_4)\text{PO}_4 \cdot 6\text{H}_2\text{O}$ —is precipitated.

This same salt is made use of for its determination also since it can be precipitated quantitatively and, on ignition, is quantitatively converted into magnesium pyrophosphate (*vide supra*).

The use of the organic reagent oxine (8-hydroxy quinoline) for the determination of magnesium is growing in favour. In suitable conditions, magnesium is precipitated as  $\text{Mg}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$ .

Magnesium also has the property of combining with certain organic dyestuffs to form deeply coloured "lakes." In particular the "lake" formed with titan yellow (or thiazole yellow) is frequently used for the detection and colorimetric determination of small concentrations of magnesium.

### § 11 Calcium, Ca. History and Occurrence

#### History

Calcium carbonate has been known since very early times in the form of minerals such as chalk, limestone and marble. Lime-burning was certainly carried on by the Romans, and it is probable that it was an old operation in their day. Chalk, quicklime and slaked lime were first clearly distinguished by J. Black in 1756. Metallic calcium was first prepared by Sir H. Davy in 1808.

#### Occurrence

Calcium does not occur free, but enormous quantities of its compounds are found. Whole mountain ranges consist of the carbonate,  $\text{CaCO}_3$ , in the forms of *chalk*, *calcite*, *limestone* and *marble*. *Dolomite*,  $\text{CaCO}_3 \cdot \text{MgCO}_3$ , also occurs in this way, while *anhydrite*,  $\text{CaSO}_4$ , and *gypsum*,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , are common minerals, and the phosphate and silicate are also found. Another important mineral is *fluorspar*,  $\text{CaF}_2$ .

Natural waters usually contain calcium salts in solution (cf. pages 308–12) and calcium compounds are also an essential constituent of plant and animal tissues, etc. Thus, bones consist largely of calcium phosphate.

### § 12 Manufacture of Metallic Calcium

Impure calcium was made by H. Davy in 1808 and the pure metal by H. Moissan in 1898 by reducing calcium iodide with sodium.

The metal is now made by electrolysis of a mixture of fused chloride and fluoride, the latter being added to lower the melting point. In G. O.

Seward and F. von Kugelgen's process (1908), the cell (Fig. 30.2) consists of a circular iron box *A* through the bottom of which projects a conical iron cathode *B* insulated from the box, at *aa*. The carbon *C*, insulated from the box, serves as anode. A water-cooled collecting ring *E* separates the metal which rises to the surface of the molten chloride. The metal accumulates until the ring is full. The top layer is cooled solid by the air, while the bottom is soft or melted. The solid part is fastened to a hook *F* which is gradually raised. The heat due to the current keeps the salt molten. The metal is protected from oxidation by the layer of fused salt.

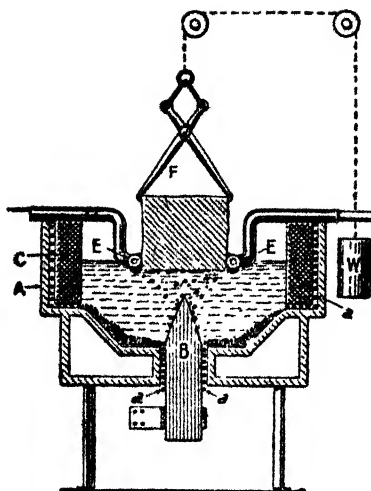


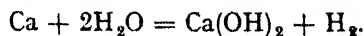
FIG. 30.2.—Production of Calcium

Crystals of almost pure calcium can be obtained by dissolving calcium in molten sodium, allowing the mixture to cool (when the calcium crystallizes out) and removing the sodium with alcohol.

### § 13 Properties of Calcium

Calcium is a silver-white lustrous metal. It is softer than most metals, and has a very low density, its specific gravity being 1.55. It melts at 850°.

Calcium is a very reactive metal. It tarnishes slowly in air, and when heated in an atmosphere of hydrogen it forms calcium hydride,  $\text{CaH}_2$ . Similarly in an atmosphere of nitrogen it forms calcium nitride,  $\text{Ca}_3\text{N}_2$ ; in air, calcium oxide,  $\text{CaO}$ , and nitride; and with chlorine, calcium chloride,  $\text{CaCl}_2$ . With water the action is rapid but not violent, and a crust of calcium hydroxide forms on the surface of the metal and slows down the reaction:



With acids the action is rather violent: calcium does not react with alkalis.

### Uses

Metallic calcium is now used fairly extensively in metallurgy as a deoxidizing and desulphurizing agent. It is also used for hardening lead in bearing alloys and for removing bismuth from lead; also for removing sulphur from petroleum. It is employed as a reducing agent, or as a dehydrating agent in organic chemistry, e.g., in the

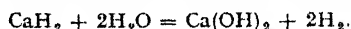
production of absolute alcohol. It is also employed in the production of high vacua, and in the preparation of argon (page 590).

### § 14 Atomic Weight of Calcium

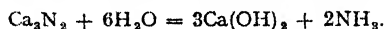
The Periodic Table and the application of Dulong and Petit's rule indicate a value of about 40 for the atomic weight of calcium. The exact value has been determined by conversion of pure Iceland spar into the oxide, and by conversion of the pure chloride into silver chloride. Hönigschmid, using the latter method (1931), obtained a value for the atomic weight very close to 40.085. The value at present (1957) recommended by the International Committee is 40.08.

### § 15 Calcium Hydride, Nitride and Carbide

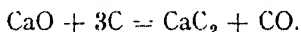
**Calcium hydride**,  $\text{CaH}_2$ , is made by passing hydrogen over heated calcium. It is a colourless, crystalline compound which has been used under the name of *hydrolith* for making hydrogen, since with water it readily yields this gas:



**Calcium nitride**,  $\text{Ca}_3\text{N}_2$ , is prepared by heating calcium in a stream of nitrogen at about  $450^\circ$ . It is a yellowish, crystalline solid which reacts with water, forming ammonia:



**Calcium carbide**,  $\text{CaC}_2$ , is made in quantity by heating a powdered mixture of quicklime and coke to a temperature of  $2000^\circ$  in an electric furnace. The action (which is endothermic) is represented:



The carbide formed is molten at the temperature of the furnace and so can be tapped off.

Calcium carbide is a hard, brittle, crystalline solid of specific gravity 2.22. When pure it is white, but commercial calcium carbide is dark grey or bronze-coloured owing to the presence of impurities. It reacts with water, forming acetylene (page 375), from which many important organic compounds are manufactured, e.g., acetone, acetic acid and acetic anhydride. When heated in an atmosphere of nitrogen to  $1000^\circ$ – $1100^\circ$  it forms **calcium cyanamide**,  $\text{CaCN}_2$ , and so furnishes a means for the fixation of atmospheric nitrogen (see pages 424, 430).



The mixture of carbon and calcium cyanamide formed is sold under the name of **nitrolim**. Calcium cyanamide is also important as the starting material for the manufacture of melamine for the plastics industry.



### § 16 Calcium Oxides and Hydroxide

Calcium forms three oxides, viz.:

Calcium oxide, or quicklime,  $\text{CaO}$ ;

Calcium peroxide,  $\text{CaO}_2$ ;

Calcium tetroxide,  $\text{CaO}_4$ ;

but only the first-named is important.

#### Calcium Oxide, Quicklime, $\text{CaO}$

Quicklime is made on a large scale by heating calcium carbonate. The reaction which takes place is reversible,



and so does not proceed to completion unless the carbon dioxide formed is allowed to escape. This reaction has been discussed (pages 244 and 245) from the standpoint of the Law of Mass Action and the Phase Rule. As stated there, there is for each temperature a value for the pressure of carbon dioxide (known as the dissociation pressure) which is in equilibrium with quicklime and calcium carbonate. Some of these values, Smyth and Adams (1923), Southard and Royster (1936), are:

Temperature:

500°	550°	600°	650°	700°	750°	800°	850°	894°	900°	950°
------	------	------	------	------	------	------	------	------	------	------

Pressure (mm. of mercury):

0.073	0.41	1.84	6.90	22.2	63.2	167	372	760	793	1577
-------	------	------	------	------	------	-----	-----	-----	-----	------

It is evident that any temperature above 500° will serve for the decomposition, provided that the carbon dioxide is removed from the system; and that at temperatures of 900° or over decomposition will be complete unless the system is confined at a pressure greater than atmospheric. In practice, a temperature of 800°–1000° is used, and the operation is carried out in a lime kiln (Fig. 30.3 A and B).

Two types of kiln are used: the older type (Fig. 30.3A) is intermittent in operation, and is rather wasteful in fuel though very cheap to install. The more modern shaft-kiln (Fig. 30.3B) is arranged for continuous operation. The limestone gradually works its way down the kiln, which is heated by producer gas, and is converted to lime which is removed at the bottom. Some forms of limestone, including chalk, are very friable and have to be burned in rotary kilns (cf. page 700).

#### Properties of Calcium Oxide

Calcium oxide, when pure, is a white amorphous powder, but as usually obtained it is in the form of hard white lumps. If heated intensely, e.g., with an oxyhydrogen blowpipe, it becomes incandescent and emits a brilliant white light. This property was formerly made

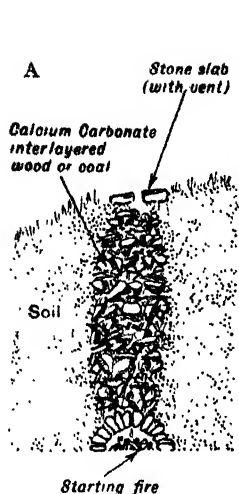


FIG. 30.3A

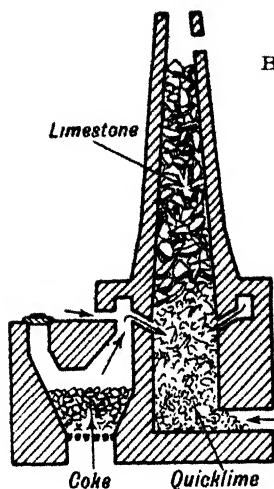
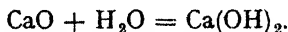


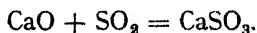
FIG. 30.3B.—Lime Kiln

use of in the "lime-light." Its melting point is  $2572^{\circ}$ , at which temperature it volatilizes appreciably.

Calcium oxide is a reactive substance, and most non-metals react with it at temperatures of  $300^{\circ}$  or over. It reacts with water at ordinary temperatures. Thus, if a few drops of water be allowed to fall on a cold lump of freshly "burnt" lime, a hissing noise is produced and clouds of steam are formed:



The lump of lime disintegrates to a fine powder of *slaked lime* or *calcium hydroxide* and the process is known as the slaking of lime. The reactivity of a specimen of quicklime has been found to depend, to some extent, on its thermal history. Calcium oxide does not react with gases such as carbon dioxide (cf. page 697) or sulphur dioxide, in the cold, but combines with them when heated, e.g.:



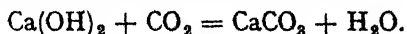
Quicklime is used in the preparation of slaked lime for building purposes (see below). It is also a constituent of cement. It is used in the laboratory for drying gases such as ammonia, which react with calcium chloride or sulphuric acid.

**Calcium peroxide**,  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ , is formed when hydrogen peroxide is added to milk of lime. Its properties are similar to those of barium peroxide (q.v.).

**Calcium tetroxide**,  $\text{CaO}_4$ , is obtained as a yellow powder by heating the hydrated peroxide with 30 per cent hydrogen peroxide solution.

**Calcium Hydroxide, Slaked Lime,  $\text{Ca(OH)}_2$** 

Slaked lime is obtained, as indicated above, by the action of water on quicklime. It is a white, amorphous powder, which is only sparingly soluble in water: 100 grams of water at  $15^\circ \text{C}$ . dissolve 0.17 gram of calcium hydroxide. It is interesting in that its solubility *diminishes* with rise of temperature, whereas the solubility of most solids increases. The solution is known as *lime-water* and has an alkaline reaction. A suspension of a considerable quantity of slaked lime in water is known as *milk of lime*. When exposed to the air lime-water soon becomes "milky" owing to the formation of insoluble calcium carbonate:



When heated to  $100^\circ$  calcium hydroxide is not decomposed, but at  $400^\circ$  30 per cent of the possible water is expelled, and at  $450^\circ$  nearly all the water can be driven off.

Calcium hydroxide reacts readily with acids and acid gases, forming salts. It also absorbs chlorine similarly (see page 548). It has been shown by J. Kalb (1867) that perfectly dry slaked lime will not absorb carbon dioxide, but that combination takes place readily in presence of a trace of moisture. This furnishes another example of the catalytic action of water (page 317).

Slaked lime is used in the laboratory for the preparation of lime-water (for the detection of carbon dioxide), and as an absorbent for chlorine and acid gases generally.

Industrially it is employed in the manufacture of bleaching powder (page 317), of caustic soda (page 615), in the ammonia-soda process (for ammonia recovery), the purification of sugar, in glass-making, and for making mortar and plaster.

**Mortar** is a thick paste made by mixing slaked lime with sand and water. It sets, on exposure to the air, by loss of water, after which it gradually hardens, by absorbing carbon dioxide with formation of calcium carbonate. This is, however, a slow process: the mortar of some Roman buildings (2000 years old) has been found to contain inner cores of slaked lime protected by the outer layers of calcium carbonate.

**Portland cement** is made by heating an intimate mixture of chalk or limestone with clay in a long, slanting cylindrical furnace, slowly rotating, through which a blast of burning coal-dust is blown (Fig. 30.4). The mixture sinters and the resulting "clinker" is ground to a fine powder. When mixed with water and sand, it forms a paste which sets in the course of a few hours, even when under water, to a solid mass which slowly grows harder over a long period. The chemical constitution of cement and the exact nature of the process which occurs when it sets are not clearly understood.

The essential constituents of the cement are believed to be a tricalcium silicate,  $3\text{CaO} \cdot \text{SiO}_2$ , and aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . When mixed with water hydration of the anhydrous salts occurs and hydrated calcium

silicate,  $2\text{CaSiO}_3 \cdot 5\text{H}_2\text{O}$ , tetracalcium aluminate,  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ , and slaked lime are supposed to be formed. These compounds crystallize out in a mass of interlacing needles which accounts for the strength and hardness of set cement.

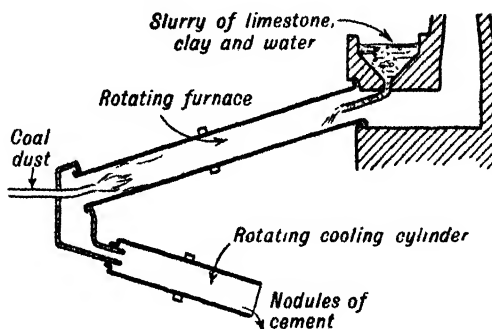


FIG. 304 - Cement Furnace

**Concrete** is made by mixing cement with sand and gravel, or broken bricks, etc., and allowing the whole to set. If it is made round a skeleton of steel rods it is known as *reinforced concrete*.

### § 17 Salts of Calcium

Calcium salts are white and give colourless solutions unless derived from a coloured acid. The majority of calcium salts are very sparingly soluble in water, the principal exceptions being the halides (other than the fluoride) and nitrate. They are not poisonous unless derived from poisonous acids. When heated in the flame of a bunsen burner, they impart to it a brick-red coloration.

#### Calcium Carbonate, $\text{CaCO}_3$

Several different minerals occur in nature which have been called different names, although analysis shows that they are all more or less impure forms of one chemical substance—calcium carbonate. These different forms of calcium carbonate may be classed under three heads, although in reality there are but two crystalline forms or mineral species.

##### 1. Calcium Carbonate in Rhombic Crystals

This variety generally occurs in needle-like crystals, and is named *aragonite* after Aragon in Spain. If calcium carbonate be prepared in solutions at temperatures exceeding  $30^\circ$ , crystals corresponding with aragonite are formed, and if at temperatures below  $30^\circ$ , crystals

of calcite are formed. Hence, aragonite at temperatures below  $30^{\circ}$  is in a metastable condition. The fundamental form of crystals of aragonite is illustrated by the outline drawing, Fig. 30.5, and although there are a great many derived shapes, all are built on the same geometrical plan determined by the inclination of the boundary faces with respect to the axes of the crystal.

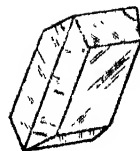


FIG. 30.5

## 2. Calcium Carbonate in Trigonal Crystals

This form of calcium carbonate occurs in more or less well-defined crystals modelled after a rhombohedron, Plate 19, but exhibiting a great variety of derived shapes which have received special names—"dog's-tooth spar," "nail-headed spar," etc. R. J. Haiiy called calcite the *proteus* among minerals because of its presenting what appeared to be a chaotic number of unrelated appearances, yet he also showed that, however diverse the forms of the crystals, they are all related to a primitive geometrical plan which is determined by the inclination of the boundary faces with the crystal axes. All the different forms are subordinate to the primitive type. When transparent and colourless, trigonal calcium carbonate is called *Iceland spar*; and if opaque and clouded, *calcite* or *calcspar*. A compact fibrous variety with a satin-like lustre is called "satin spar." *Marble* is made up of minute crystals of calcite. *Onyx marble* is a variety which is streaked and coloured by associated impurities.

## 3. Calcium Carbonate not markedly Crystalline

Chalk and limestone usually occur in large masses sometimes extending over large tracts of country. This form of calcium carbonate is relatively impure, for it contains more or less magnesium carbonate, clay, and silica. Marl is a mixture of limestone and clay. Egg-shells, sea-shells, pearls, corals contain a large percentage of calcium carbonate. *Chalk* consists largely of the calcareous remains of minute marine organisms.

H. C. Sorby proved that in calcareous organisms a new variety of calcium carbonate is not in question. In every case examined, the shells contained either calcite or aragonite. Some animal species secrete calcium carbonate as calcite, others as aragonite, and others as both. The pearl, for instance, is mainly aragonite; the shell of the common whelk is mainly calcite; and the inner shell of the cuttlefish is aragonite, the outer portion is calcite.

Calcium carbonate is almost insoluble in water alone, but is soluble in the presence of carbon dioxide owing to the formation of the bicarbonate. When heated it decomposes into calcium oxide and carbon dioxide; a reaction discussed more fully on pages 244, 697. It is readily attacked by acids with liberation of carbon dioxide; if the acid used forms an insoluble calcium salt, the reaction may stop owing to the

formation of a protective "skin" unless the carbonate is very finely divided.

Calcium carbonate is used in the manufacture of whiting (which is chalk ground to powder and freed from sandy impurities by levigation in water), in the manufacture of quicklime (and hence of slaked lime and of cement); as a flux in the smelting of iron and in metallurgy generally, and in the manufacture of sodium carbonate. *Nitro-chalk* used as a fertilizer, is a mixture of ammonium nitrate and powdered chalk. In the precipitated form calcium carbonate is employed medicinally and in the preparation of toothpastes.

Chalk and marble are also used in the laboratory as sources of carbon dioxide.

**Calcium bicarbonate**,  $\text{Ca}(\text{HCO}_3)_2$ , is formed in solution by the action of carbon dioxide and water on the normal carbonate. It cannot be isolated, and even in solution decomposes on heating. Its presence in natural waters causes temporary hardness (cf. page 308).

### Calcium Fluoride, $\text{CaF}_2$

Calcium fluoride occurs naturally as *fluorspar* in many places, sometimes (e.g., in Derbyshire) veins of fine crystals are found embedded in limestone. The crystals may be colourless, or tinted by traces of contaminating metallic oxides. "Blue-john" is a familiar example of a tinted variety.

When heated to about  $1360^\circ$ , fluorspar melts to an opaque greyish-white enamel, and its name is derived from this property (Latin *fluere*, to flow). It is used as a flux in metallurgy, and in the manufacture of glass, enamels and glazes. It is also the principal source of fluorine compounds (Chapter 26). Some of the coloured varieties are used for jewellery, ornamental vases, etc.

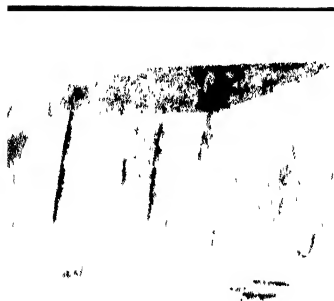
### Calcium Chloride, $\text{CaCl}_2$

This salt is obtained as a by-product in the ammonia-soda process, but so far it has not been found possible to discover uses for it in quantity comparable with the amount produced. Considerable quantities are used by the refrigeration trade for circulating "brine" (cf. page 432); a good deal is used in concrete-making and in the building industry and among other uses are dyestuffs manufacture (alizarin), fireproofing, dust-laying, road-making, weedkillers, domestic glue mixes and china glazes. The anhydrous salt is used in the laboratory as a drying agent for many gases and liquids. (It cannot be used to dry ammonia as this gas combines with it, forming compounds such as  $\text{CaCl}_2 \cdot 8\text{NH}_3$ .)

The anhydrous salt is a white porous mass, extremely deliquescent, and very soluble in water: 100 grams of water will dissolve 63 grams of the anhydrous salt at  $10^\circ$ . Calcium chloride forms several hydrates; the hexahydrate being the stable one at ordinary temperatures.



18 Crystals of aragonite  
from Cumberland



19 Crystals of calcite



20 Crystals of antimony



Austenite



Sorbite



Pearlite



Cementite



Martensite

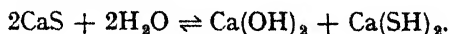


**Calcium nitrate**,  $(\text{CaNO}_3)_2$ , occurs in the soil and is used as a fertilizer. It is manufactured from limestone and dilute nitric acid. It is often known as *Norwegian saltpetre* since it was a product of the (now obsolete) Birkeland-Eyde process for the fixation of nitrogen which used to be worked in Norway.

### Calcium Sulphide, $\text{CaS}$

This substance has been produced in very large quantities in the form of the "alkali-waste" of the Leblanc process (q.v.). It can also be made by heating slaked lime in an atmosphere of hydrogen sulphide; or by reducing the sulphate with carbon. When pure it is a white powder, which is stable in air in absence of moisture. It exhibits a very marked phosphorescence (although only if a minute trace of a metallic impurity, e.g., bismuth, be present. The function of the metal in promoting the phosphorescence is not understood.)

Calcium sulphide is hydrolysed by water, forming a mixture of hydroxide and hydrosulphide:



When exposed to the air calcium sulphide emits an odour of hydrogen sulphide; probably this gas is formed in small quantity through the action of carbon dioxide in presence of moisture. This behaviour rendered the great heaps of "alkali waste" produced by the Le Blanc process, before the development of methods for the recovery of the sulphur, particularly obnoxious (cf. page 619).

**Calcium hydrosulphide**,  $\text{Ca}(\text{SH})_2$ , is made by passing hydrogen sulphide into milk of lime. It is used in tanning for removing the hair from hides

### Calcium Polysulphides, $\text{CaS}_n$

When milk of lime is boiled with sulphur, the sulphur dissolves and calcium polysulphides are formed. It is supposed that the **tetrasulphide** and thiosulphate are first formed:



and that the latter decomposes into sulphite and sulphur, while the former forms the **pentasulphide** with excess of sulphur.

### Calcium Sulphate, $\text{CaSO}_4$

This occurs native, as *anhydrite*,  $\text{CaSO}_4$ ; and as *gypsum*,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . If the gypsum occurs in clean, fine-grained masses it is called *alabaster*; if in translucent crystals, it is known as *selenite*.

The dihydrate may also be prepared by mixing solutions of sulphates with solutions of calcium salts, or by treating calcium carbonate or hydroxide with dilute sulphuric acid.

Calcium sulphate is sparingly soluble in water: 100 grams of water dissolve 0.19 gram of anhydrous salt at  $0^\circ$ . The solubility increases with rise of temperature up to  $40^\circ$  after which it falls again. This causes the formation of very hard scale in boilers when calcium sulphate is

present in the feed water. The presence of calcium sulphate in natural waters causes permanent hardness (page 308).

### Plaster of Paris

When gypsum is heated to about  $120^{\circ}$  it loses the equivalent of  $1\frac{1}{2}$  molecules of water and forms the so-called hemi-hydrate,  $(\text{CaSO}_4)_2\text{H}_2\text{O}$ . This substance is known as *plaster of Paris* because of the large deposits of gypsum used for the manufacture of plaster at Montmartre (Paris).

When plaster of Paris is wetted with, say, one-third of its weight of water, it forms a plastic mass which "sets" in from 5 to 15 minutes to a white, porous hard mass. A slight expansion occurs during the setting, so that it will take a sharp impression of a mould. The setting is due to the formation of an interlacing mass of fine needles of the dihydrate which take up more room. Admixture of alum or borax with the plaster reduces the rate of setting, while common salt accelerates it. Alum makes a plaster which when set is much harder; the mixture of plaster of Paris with alum is known as *Keene's cement*.

If plaster of Paris, or gypsum, be heated above  $200^{\circ}$  it passes into anhydrous calcium sulphate which does not set when mixed with water, since it takes up water only very slowly. This is known as *dead-burnt plaster*.

**Calcium bisulphite**,  $\text{Ca}(\text{HSO}_3)_2$ , obtained in solution by saturating milk of lime with sulphur dioxide, is extensively employed for dissolving the lignin of wood pulp for paper-making, and as an antiseptic in brewing.

**Calcium silicate**,  $\text{CaSiO}_3$ , occurs naturally as *wollastonite*. It is an important constituent of glass (page 778), cement (page 699), and furnace slag (page 904) and is used as a reinforcing filler for rubber, both natural and artificial, and for some plastics.

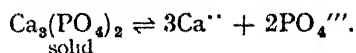
### Calcium Phosphates

The phosphates of calcium are amongst the most important of the salts of phosphoric acid. Pure crystalline **tricalcium phosphate**,  $\text{Ca}_3(\text{PO}_4)_2$ , has not been obtained. The nearest approach to it is made by adding sodium phosphate to a solution of calcium chloride in presence of ammonia. Several more or less impure forms of calcium phosphate occur in nature, e.g., *apatite*; and calcined bones contain 60 to 80 per cent of the normal phosphate.

Normal calcium phosphate is very sparingly soluble in water: 100 grams of water dissolve 0.002 gram at  $20^{\circ}$ . The presence of alkalis decreases the solubility, while neutral salts and acids increase it. Thus calcium phosphate passes into solution\* when treated with dilute

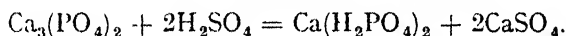
\* Objection is sometimes raised to the use of the word *soluble* to describe the behaviour of calcium phosphate with mineral acid and similar reactions in which the solution is the result of chemical action. Many prefer to restrict the terms *dissolve*, *soluble*, etc., to purely physical processes; but it is not always easy to draw the line between physical and chemical "solution."

acids, but is reprecipitated on addition of alkali. This behaviour is explained by the Ionic Theory as follows. The calcium phosphate furnishes calcium ions and phosphate ions



Phosphoric acid is a very weak acid, i.e., it ionizes only to a very slight extent in solution. The addition of a dilute solution of a strong acid increases very largely the hydrogen ion concentration and hence removes phosphate ions from the solution as non-ionized phosphoric acid. This disturbs the equilibrium between the calcium phosphate and its ions, so causing more to dissolve. On adding alkali to this solution, the hydrogen ions are removed, more phosphate ions are formed, thus exceeding the solubility product of calcium phosphate, which is accordingly reprecipitated.

Calcium phosphate is an important fertilizer, but its action is very slow on account of its small solubility. To convert it into a more soluble acid salt it is treated with sulphuric acid—usually chamber acid—in order to turn it into **monocalcium phosphate**.



The acid phosphate becomes  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and the sulphate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . This mixture, which is called **superphosphate**, usually contains a little undecomposed normal phosphate.

Another form in which calcium phosphate is obtained is the **basic slag** of the basic Bessemer, and open-hearth processes for steel-making (page 908). It probably consists mainly of calcium silico-phosphate,  $\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaSiO}_3$ . It is an important fertilizer.

**Calcium oxalate**,  $\text{Ca} \begin{array}{l} \text{O.OC} \\ | \\ \text{O.OC} \end{array}$ , is a very sparingly soluble substance

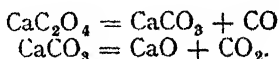
and is used for the estimation of calcium (see below). It is obtained as a white precipitate on addition of ammonium oxalate solution to a soluble calcium salt in presence of ammonia. Mineral acids act upon it in a manner similar to their action on calcium phosphate (*vide supra*), thus causing it to dissolve. Calcium oxalate is re-formed as a precipitate on addition of alkali.

### § 18 Detection and Determination of Calcium

Calcium salts may be detected by the brick-red colour which, when moistened with hydrochloric acid, they impart to the bunsen flame—provided that strontium, barium and sodium are absent.

In qualitative analysis calcium, strontium and barium salts are precipitated as carbonates by ammonium carbonate in presence of ammonia. The qualitative separation of these three metals is discussed on page 711.

Calcium is usually determined as oxalate, by adding a boiling solution of ammonium oxalate to a solution of the calcium salt to which ammonia and ammonium chloride have been added. After washing and drying, the precipitate is ignited: if carried out carefully the product is the carbonate, strong ignition yields the oxide:



Alternatively, the precipitate can be dissolved in warm dilute sulphuric acid and the oxalic acid so liberated titrated with potassium permanganate (page 894).

### § 19 Strontium, Sr

#### History

A strontium mineral was probably first distinguished in 1791 by Hope, when examining the minerals found in a lead mine at Strontian in Argyllshire. One of these, which was also examined by Kirwan and by Klaproth in 1793, was concluded to be the carbonate of a new earth to which the name *strontia* was given. Strontium was first isolated by Davy in 1808.

#### Occurrence

Strontium occurs as the carbonate (referred to above) and known as *strontianite*; and also as the sulphate, *celestine*. Strontium also occurs in small quantities associated with other alkaline earth minerals. Strontium is much scarcer than either calcium or barium.

For the **preparation** of metallic strontium, similar methods can be employed to those used for calcium. Usually it is obtained by electrolysis of the fused chloride.

In its **properties** strontium resembles calcium. It is a white metal of low specific gravity (2.6) and is chemically more reactive than calcium.

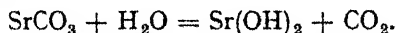
So far no **uses** have been found for the metal as such, although its employment in photo-electric cells has been suggested. Some of its compounds have commercial uses, however, e.g., the hydroxide in sugar-refining and the nitrate in firework-making, for "red fire," etc.

The **atomic weight** of strontium is in the neighbourhood of 88. This is in agreement with its place in the Periodic Table and with its specific heat. The exact atomic weight has been determined by methods similar to those used for calcium. Richards, by conversion of the bromide into silver bromide, and of the chloride into silver chloride, obtained values between 87.620 and 87.629. The value recommended by the International Committee is 87.63.

## § 20 Compounds of Strontium

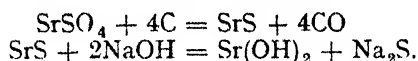
Strontium compounds closely resemble those of calcium; as a rule the salts of strontium are the less soluble. Strontium salts, moistened with hydrochloric acid, impart a brilliant crimson colour to the flame of a bunsen burner.

**Strontium oxide**,  $\text{SrO}$ , is made on a large scale by heating the carbonate in superheated steam: carbon dioxide is evolved and strontium hydroxide is formed:



The hydroxide on ignition furnishes the oxide. The temperature required for the direct decomposition of the carbonate to the oxide is higher than in the case of calcium.

Strontium oxide is also made commercially from celestine by heating it with carbon and treating the sulphide formed with caustic soda. The sodium sulphide is removed by means of water and the strontium hydroxide converted into the oxide by heating:



Strontium oxide resembles quicklime. It "slakes" similarly on addition of water.

**Strontium hydroxide**,  $\text{Sr(OH)}_2$ , which may be made from celestine as described above, resembles slaked lime, but is more soluble in water: 100 grams of water will dissolve 0.81 gram of strontium hydroxide at  $20^\circ$ . It is a stronger base than slaked lime. It is extensively used in sugar-refining since it combines with cane sugar, forming an insoluble *saccharate*, from which the sugar can be regenerated by carbon dioxide, strontium carbonate being precipitated. Thus by its use a further quantity of sugar can be extracted from the "molasses" left after the first crop of sugar has crystallized out.

**Strontium peroxide**,  $\text{SrO}_2$ , can be made by the action of hydrogen peroxide on strontium oxide and also by direct combination of the metal with the oxygen of the air at 150 atmospheres pressure and a temperature of  $500^\circ$ . It is sometimes used in the burning mixture for tracer bullets.

**Strontium carbonate**,  $\text{SrCO}_3$ , occurs native as *strontianite* and is made commercially from celestine by fusion with sodium carbonate. It resembles calcium carbonate, but is less easily decomposed by heat.

**Strontium nitrate**,  $\text{Sr(NO}_3)_2$ , is made technically by precipitation from concentrated solutions of strontium chloride and sodium nitrate. (Cf. preparation of potassium nitrate from Chile saltpetre, page 641.) It is extensively used in pyrotechny for "red fires."

**Strontium sulphate**,  $\text{SrSO}_4$ , occurs naturally as *celestine*. It differs from calcium sulphate in being less soluble in water and insoluble in

ammonium sulphate. It closely resembles barium sulphate in most of its chemical properties.

**Strontium chloride**,  $\text{SrCl}_2$ , is made commercially by the action of calcium chloride on strontium carbonate. It resembles calcium chloride in being very soluble in water (100 grams of water dissolve 50 grams of anhydrous salt at  $15^\circ$ ); it forms a similar hexahydrate, but it is not so hygroscopic.

## § 21 Barium, Ba. History, Occurrence and Extraction

### History

V. Casciorolus, in 1602, noticed that when heavy spar was calcined with combustible matters, the product became phosphorescent in the dark. He called the stone *lapis solis*, and later, it was called "Bolognian," or Bononian phosphorus. The heavy spar which furnished *lapis solis* was at first believed to be a peculiar kind of gypsum. K. W. Scheele (1774) found that the mineral contained a new earth which gave a sulphate insoluble in water. G. de Morveau called the earth "barote"—from the Greek *βαρύς* (*barus*), heavy—and Lavoisier later altered the word to "baryta," the name now used for this earth.

### Occurrence

The principal barium mineral is the sulphate, known as *heavy spar* or *barytes*. The carbonate also occurs and is known as *witherite*; while an impure barium manganite,  $\text{BaO} \cdot \text{MnO}_2$ , is known as *psilomelane*.

### Preparation and Properties

Metallic barium, in the form of an amalgam with mercury, was first obtained by Davy in 1808. It is one of the most difficult metals to prepare. It has been obtained by electrolysis of barium chloride using a mercury cathode; the barium is recovered by distilling off the mercury from the amalgam. It has been claimed that it is not possible to obtain pure barium in this way and that the best method is to reduce the oxide with metallic aluminium and to distil the product (Guntz, 1929).

Barium is a silvery white metal, resembling calcium in appearance. It is soft, of specific gravity 3.5, and m.p.  $704^\circ$ . It is very reactive and inflames spontaneously if exposed to the air when finely divided. Its reactions are similar to but more vigorous than those of calcium.

## § 22 Atomic Weight of Barium

The principal determinations of the atomic weight of barium have been made by conversion of the chloride into the sulphate, or of the chloride or bromide into the corresponding silver salt. Richards, using these latter methods, obtained values between 137.34 and 137.38. Hönigschmid in 1929, working similarly, obtained a slightly lower

value than the mean of Richards's work. The value at present (1955) recommended by the International Committee is 137.36.

### § 23 Barium Oxides and Hydroxides

The principal oxides of barium are:

Barium oxide, BaO;  
Barium peroxide, BaO<sub>2</sub>;

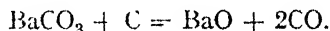
whilst a third,

Barium suboxide, Ba<sub>2</sub>O,

has been reported.

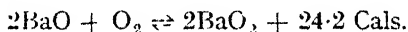
#### Barium Oxide, Baryta, BaO

Barium oxide is often made by decomposing the hydroxide or nitrate at a red heat as the carbonate requires a very high temperature for its decomposition. If the carbonate is to be used, it is mixed with lampblack or tar before heating. The carbon burns off and the carbonate, at the same time, is decomposed at a much lower temperature:



Barium oxide is a white powder which slakes in contact with water, so much heat being evolved that, if but a little water be used, the mass may become visibly red hot. When heated in air, some barium peroxide is also formed (q.v.).

**Barium peroxide**, BaO<sub>2</sub>, results when barium oxide is heated in air to 400° or over:

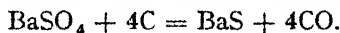


The reaction is reversible, and since its formation involves the evolution of heat and reduction of volume, a rise in temperature or decrease of pressure will favour the decomposition of the peroxide. This fact was made use of in the now obsolete Brin's process for the manufacture of oxygen (page 334). Barium peroxide is also formed by the action of hydrogen peroxide on a solution of barium hydroxide. When made in this way it crystallizes out as BaO<sub>2</sub>.8H<sub>2</sub>O.

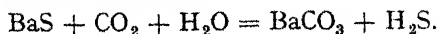
Barium peroxide is a white insoluble powder, which reacts with acids, forming hydrogen peroxide in the cold (page 321); or oxygen at higher temperature. It was formerly used for the manufacture of hydrogen peroxide.

#### Barium Hydroxide, Ba(OH)<sub>2</sub>

Barium hydroxide results from the slaking of barium oxide. Commercially, it is made by heating a mixture of barytes with powdered coke or coal, when crude barium sulphide is formed:



The latter is then heated in a stream of carbon dioxide, and thus converted into barium carbonate:



The carbonate is converted into the hydroxide by heating in superheated steam as described for strontium hydroxide (page 707). Sometimes the native carbonate, witherite, is treated similarly.

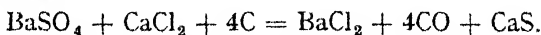
Barium hydroxide is a white powder which, unlike calcium hydroxide, can be fused without decomposition. It melts at  $325^\circ$  and decomposes if heated to from  $600^\circ$  to  $1000^\circ$ . It is much more soluble in water than either calcium or strontium hydroxide: 100 grams of water dissolve 3.23 grams of barium hydroxide at  $15^\circ$ . The solution, which is strongly alkaline, deposits crystals of  $\text{Ba}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . Barium hydroxide is used for the titration of weak acids in volumetric analysis, since it is the only reasonably soluble strong base which (owing to the insolubility of its carbonate) is always free from dissolved carbonate.

### § 24 Salts of Barium

Barium salts are white unless derived from a coloured acid, and give colourless solutions. They are poisonous. They are for the most part insoluble or only very sparingly soluble; the principal soluble ones being the nitrate and chloride. When moistened with hydrochloric acid, and heated in the flame of a bunsen burner, they give it an apple-green coloration.

**Barium carbonate**,  $\text{BaCO}_3$ , occurs naturally and is also made commercially from barytes, as described under barium hydroxide. It is a white powder resembling chalk in many respects, insoluble in water, dissolving to a small extent in presence of excess of carbon dioxide. It does not decompose on heating at atmospheric pressure below a temperature of  $1450^\circ$ . Mixed with charcoal (60 : 40) it is used in the case-hardening of steel.

**Barium chloride**,  $\text{BaCl}_2$ , is made either from the carbonate or from the crude sulphide resulting from reduction of the native sulphate, by dissolving in hydrochloric acid. Technically it is also made by strongly heating a mixture of barytes with coke and calcium chloride, followed by lixiviation with water to extract the barium chloride which is soluble:



The aqueous solution deposits crystals of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ .

The anhydrous salt is a white solid, the hydrated crystals are colourless and transparent. Neither anhydrous nor hydrated salt is deliquescent, in marked contradistinction to calcium chloride. Barium chloride is soluble in water: 100 grams of water dissolve 34.4 grams of anhydrous salt at  $15^\circ$ .

Barium chloride is extensively used in analysis for the detection and determination of sulphates (page 508).



**Barium nitrate**,  $\text{Ba}(\text{NO}_3)_2$ , is usually made by mixing solutions of sodium nitrate and barium chloride. (Compare the preparation of potassium nitrate, page 641.) It forms colourless crystals, which are fairly soluble in water: 100 grams of water dissolve 8.7 grams at  $20^\circ$ . It is used for the preparation of the oxide, and for making "green fire" for fireworks.

**Barium sulphide**,  $\text{BaS}$ , is made on a large scale by reduction of barytes for the preparation of other barium compounds. In presence of minute traces of impurities, it exhibits marked phosphorescence like calcium sulphide and like which it was formerly used in making luminous paints. It is extensively used for the manufacture of lithopone (q.v., page 720).

**Barium sulphate**,  $\text{BaSO}_4$ , occurs native as *barytes* or *heavy spar*. It is formed as a heavy white precipitate on mixing solutions of a soluble barium salt and a soluble sulphate. It is a white solid, unaffected by heat below  $1500^\circ$ , and is extremely sparingly soluble in water. With concentrated sulphuric acid the acid sulphate is formed,  $\text{Ba}(\text{HSO}_4)_2$ , which is moderately soluble in water. It is reduced to the sulphide by heating with carbon as already mentioned; and is decomposed to some extent when fused with sodium carbonate in excess:



It is used in the manufacture of paint by the name of *permanent white*, also as a "filling" for rubber and for paper-making, to increase the opacity and weight of the paper.

### § 25 Detection and Determination of Barium

Barium is frequently detected by the formation of the insoluble sulphate in presence of hydrochloric acid on addition of a solution of a soluble sulphate. It is generally determined by the same method.

In qualitative analysis barium is usually precipitated along with calcium and strontium by addition of ammonium carbonate solution to the solution (containing ammonia and ammonium salts) remaining after removal of metals whose chlorides, sulphides and hydroxides are insoluble.

Several methods are in use for the separation of the mixed carbonates so obtained, of which the following is fairly representative, and depends upon the facts that barium chromate is insoluble in acetic acid, while strontium chromate is soluble in it and calcium chromate is appreciably soluble in water; and also that calcium sulphate is soluble in presence of acid in concentrated ammonium sulphate solution, whereas strontium sulphate is not.

The carbonates are dissolved in the minimum of dilute acetic acid; the solution is boiled and potassium chromate added until no more barium chromate is precipitated. The filtrate from this precipitate is mixed with two-thirds of its volume of concentrated hydrochloric

acid, then treated with its own volume of ammonium sulphate solution, and left to stand for ten minutes. Any strontium sulphate formed is filtered off, and the filtrate made alkaline with ammonia solution. The addition of boiling ammonium oxalate solution precipitates any calcium present as oxalate.

### § 26 Radium

Radium, with Atomic Number 88, is the last member of the alkaline earth family of elements and is one of the most important of the radio-elements. It is a very rare element; the principal source is pitchblende where it is formed as a result of the radioactive disintegration of uranium, but since it has a half-life period of 1590 years whereas that of uranium is  $4.5 \times 10^9$  years the amount of radium present at equilibrium is extremely small, being of the order of 150 milligrams per ton. The theoretical ratio, calculated from the half-life periods, would be about 345 milligrams of radium per ton of uranium.

Radium was discovered in 1898 by Madame Curie as a consequence of the observation that the radioactivity of some uranium minerals (notably Joachimsthal pitchblende) is much greater than corresponds to the uranium present. This extra activity she traced to the presence of a new radioactive element of high activity, to which the name radium was given.

#### Extraction

The extraction of radium is a very long and laborious process on account of the minute amount present in the ore. Pitchblende is roasted with sodium carbonate and then digested with dilute sulphuric acid when the uranium goes into solution and the residue is boiled with sodium hydroxide solution and washed with water. The portion remaining undissolved is treated with hydrochloric acid after which a very small residue which remains is boiled with sodium carbonate solution. The resulting carbonates are dissolved in hydrobromic acid, from which a mixture of barium and radium bromides is obtained. The radium bromide is finally obtained pure by fractional crystallization. Some ores contain substantial quantities of silver; when this is the case the silver is extracted from the sulphate precipitate by means of sodium thiosulphate solution.

Metallic **radium** was first obtained by Madame Curie and Debierne in 1910 by the electrolysis of a solution of the chloride using a mercury cathode. The radium was recovered by distilling off the mercury.

#### Properties and Uses

Radium is a silvery white metal which melts at  $700^{\circ}$ ; it tarnishes rapidly in air on account of the formation of the nitride. It decomposes water with liberation of hydrogen.

The **salts of radium** are isomorphous with the corresponding salts of barium and are colourless (unless the anion is coloured). They impart a carmine colour to the bunsen flame. They are less soluble than the corresponding barium salts.

**Radium bromide**,  $\text{RaBr}_2$ , is the most important salt of radium. It is used in medicine, as a source of  $\alpha$ -rays for the localized treatment of malignant growths, although radon (q.v., page 595) is now more frequently used for this purpose, radium bromide being the common source of the radon. Small amounts of radium salts are used for the luminous coating of watch dials and aircraft instruments. For this purpose a minute trace of the radium is mixed with zinc sulphide which fluoresces owing to the presence of the radium.

## CHAPTER 31

# ZINC, CADMIUM AND MERCURY

### § 1 Zinc, Zn. History and Occurrence

#### History

Brass, an alloy of zinc and copper, was known to the ancients, and several references to brass occur in the sacred writings. R. Jagnaux says that bracelets made of zinc have been found in the ruins of Cameros which was destroyed about 500 B.C. The word "zinken" appears in the writings ascribed to Basil Valentine, but it is not there referred to as a metal, and it seems to be confused with several other substances. Paracelsus also uses the word in the sixteenth century. At that time the term *zinc* appears to have been employed locally by the miners in the Carnia for an earthy ore. Near the beginning of the seventeenth century, zinc was brought from China and the East Indies under the name "tutanego," Indian tin, calamine, or speauter. Libavius (1597) said that the Indian tin and the Goslar metal were the same. About this time, however, there was much confusion as to the meaning of zinc. In 1697, Lohneyes appears to have been the first definitely to apply the term "zink" to the metal now known as zinc. In 1695 W. Homberg, and in 1721 J. F. Henkel, discovered that zinc could be obtained from calamine, and a works for the manufacture of zinc was erected at Bristol about 1740 by J. Champion.

#### Occurrence

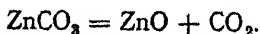
Metallic zinc has been reported in the basaltic rocks of Victoria (Australia); but it usually occurs combined: as carbonate, *zinc spar*, *calamine*,  $\text{ZnCO}_3$ ; sulphide, *zinc blende* or *black jack*,  $\text{ZnS}$ ; oxide, *zincite* or *red zinc ore*,  $\text{ZnO}$ ; silicate, *willemite*,  $2\text{ZnO} \cdot \text{SiO}_2$ ; *franklinite*,  $(\text{ZnFe})\text{O} \cdot \text{Fe}_2\text{O}_3$ ; *zinc spinel* or *gahnite*,  $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ .

### § 2 Extraction of Zinc

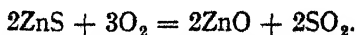
The principal ore of zinc used for the manufacture of the metal is the sulphide; often in the form of a concentrate from which ores of lead, etc., have been removed. (Cf. page 600.) The carbonate is also used to some extent.

The process of extraction involves two operations, viz., (i) *roasting* to convert the ore to the oxide; and (ii) *reduction* to the metal.

The *roasting* of the carbonate presents no difficulty, carbon dioxide being driven off:

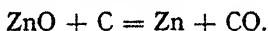


In the case of sulphide ores the sulphur is oxidized to sulphur dioxide by calcination in air. This is now effected in roasters in which the burning is carried out on a large continuous moving "belt" on to one end of which the ore is fed. It then passes under a large hood where, while being heated by an oil flame, air is sucked through it. The sulphur dioxide passes up the hood to be used for sulphuric acid manufacture by the contact process (page 501), and the zinc oxide falls off the end of the "belt."

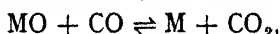


The manufacture of zinc and sulphuric acid are in this way carried on side by side.

For the *reduction* of the roasted ore, it is mixed with crushed coke or anthracite and heated to 1400°–1450° in fireclay retorts. The heating is usually effected by producer gas using regenerative furnaces for the recovery of the waste heat, similar to those employed in gas-works and coke-oven practice (pages 378, 387). The oxide is reduced with the formation of carbon monoxide:



Most metallic oxides are reduced by a reaction of the type



which is reversible; but usually the concentration of carbon dioxide necessary for the right-to-left reaction to be appreciable is very high. In the case of zinc vapour and carbon dioxide, however, the back reaction is marked and hence to complete the reduction of the zinc oxide in the retort it is necessary to use excess of carbon and so prevent the formation of carbon dioxide. The temperature required for the reduction is considerably above the boiling point of zinc, which therefore distils over and is collected in "condensers" and receivers of fireclay or iron. At first, a bluish-grey powder collects in the receiver—known as *zinc dust*—but later the metal condenses to a liquid which is drawn off at intervals and cast into blocks—known as *spelter*. The spelter formed in the earlier stages of a distillation is pure enough for commercial use—the later portions require further purification, e.g., by liquation to separate it from lead, or by distillation. The retorts used in zinc manufacture differ to some extent in different works, but have the same main characteristics. A typical retort is illustrated in Fig. 31.1. It is of elliptical section and measures 8 in. by 11 in. inside and is about five feet long. These retorts are arranged in furnaces in three or four tiers; an average "bank" comprising some 300 retorts.

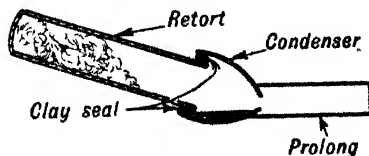


FIG 31.1 —Zinc Retort

Recently there has been considerable development of the use of

vertical retorts, which have the advantage of continuous operation. These retorts are rectangular, about 6 ft. by 1 ft. by 25 ft. high, and are made of silicon carbide bricks. They are provided with an extension at the top into which the charge is fed and preheated and another at the bottom for the removal of the ash through a water seal. The charge consists of briquettes about 4 in. long made from roasted zinc ore and powdered coal. The retorts are heated, by means of gas flames, in a large chamber of refractory material, to a temperature of 1400°. The zinc vapour and carbon monoxide formed pass up and into condensers from which the molten zinc flows to a sump. The carbon monoxide is used for heating the retorts. As well as having the advantage of continuous operation this method obviates loss of zinc through the reaction



since the formation of  $\text{CO}_2$  is largely prevented.

Zinc is now refined by redistillation under reduced pressure and considerable quantities of the metal of 99.97 per cent purity are produced in this way.

Considerable developments have also taken place in the electrolytic manufacture of zinc. The stages in this process are:

(i) Roasting of the raw ore, as before; (ii) dissolving out the zinc oxide, using spent electrolyte (sulphuric acid) from stage iv; (iii) removal of impurities which interfere with electrolysis, or would contaminate the product, e.g., iron, silica, arsenic, antimony, copper, cadmium and cobalt; (iv) electrolysis of the zinc sulphate solution using aluminium sheets as cathodes, and lead anodes: this results in the re-formation of sulphuric acid in solution, (v) melting the cathode zinc and casting into ingots.

By this process also zinc can be manufactured of a purity of 99.97 per cent.

A process for the smelting of zinc in a blast furnace has been developed successfully recently. This method is likely to find increasing use, especially as it can be used with a mixed zinc-lead ore with recovery of both zinc and lead without using any more carbon for the reduction than would be required to obtain the zinc alone. This is because the lead oxide is reduced by the carbon monoxide formed by the action of the carbon on the zinc oxide.

As stated already, when zinc oxide is reduced to the metal with carbon, the temperature required is above the melting point of zinc which is therefore liberated as a vapour; the problem of adapting the blast furnace to the production of zinc is to find a way of recovering the zinc from the exit gases of the furnace. This problem has been solved by removing the zinc with molten lead.

The blast furnace is charged with a mixture of sintered, roasted concentrates (either zinc or zinc lead) and coke. The furnace gases which contain 5 to 6 per cent of zinc are brought into contact with a shower of molten lead. The zinc is condensed and recovered as molten

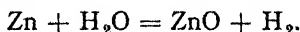
metal since, after cooling somewhat, it forms a liquid layer on the surface of the molten lead with which it is immiscible. If a charge containing lead is being smelted, molten lead is also tapped from the bottom of the furnace.

The gases, after removal of zinc, consist mainly of carbon monoxide and are used for heating the blast, preheating the charge and for other energy requirements of the process in general.

### § 3 Properties of Zinc

Zinc is a bluish-white metal, of sp. gr. about 7.1, being thus a little less dense than iron. It is brittle at ordinary temperatures, loses its brittleness about 120°, but regains it at 200° when it can be readily powdered. As cast, zinc has a crystalline structure and if it be melted and poured on to a non-conducting surface of, say, asbestos, and the liquid portion run off from that which first solidifies, a residue of hexagonal pyramidal crystals will be obtained. Zinc melts at 419.5° and boils at 907°. It is a good conductor of heat and electricity.

Zinc is slowly oxidized in moist air; and in water containing air in solution, basic carbonates are formed. When heated to about 1000°, zinc burns in air with a bluish-white flame forming a bulky mass of zinc oxide known as *philosopher's wool*. It also reacts readily with chlorine and sulphur. Pure zinc is not attacked by water at the boiling point, but commercial zinc reacts slowly; at a red heat zinc easily decomposes steam:



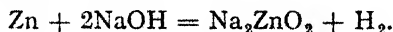
Zinc containing impurities is readily attacked by dilute acids with evolution of hydrogen in most cases, though not with nitric acid (cf. pages 288 and 452). Pure zinc, however, reacts with acids only very slowly if at all. This is thought to be because the impurities in commercial zinc form small galvanic "cells" with the zinc which passes into solution in consequence; whereas with pure zinc no "cells" are formed.

Nitric acid yields zinc nitrate, but the nature of the other product depends upon the concentration of the acid. With concentrated acid, nitrogen peroxide is the principal product; with a somewhat weaker acid, nitric oxide; and with dilute acid, ammonia is formed which is not evolved but remains behind as ammonium nitrate. With dilute acid of the right concentration, nitrous oxide may be formed.

Dilute sulphuric acid gives hydrogen with zinc (cf. page 288) but hot concentrated sulphuric acid yields sulphur dioxide (page 506).

Zinc in presence of an acid such as dilute hydrochloric or sulphuric acid is a very good reducing agent (see page 293)—nascent hydrogen being more effective than gaseous hydrogen.

Zinc will also react with hot concentrated alkali solutions, evolving hydrogen and forming a solution of sodium zincate, e.g.:



Zinc is a very electropositive metal, being high in the electro-chemical series (page 231) and, in consequence, will displace many other metals from solutions of their salts. It is used for this purpose in the extraction of gold and silver by the cyanide method (pages 674 and 664).

#### § 4 Uses of Zinc

Zinc is used in large quantities in making electric batteries, and certain utensils. Sheets of zinc have also been employed for roofing purposes, but on account of its softness galvanized iron (see below) is more often employed.

The principal use of zinc is in the manufacture of *galvanized iron*, which is iron covered with a layer of zinc to prevent rusting. It is made by dipping iron, cleaned by "pickling" in dilute hydrochloric acid, into molten zinc. The zinc protects the iron from rusting, and unlike tin, the protection is effective even if the zinc coating becomes broken. This is because zinc is a more electropositive metal than iron and hence is attacked first. Iron articles may also be coated with zinc by heating them and spraying them with zinc-dust. This is known as *sherardizing*.

Zinc alloyed with 4 per cent of aluminium, up to 3·5 per cent of copper and 0·05 per cent of manganese is largely used for the production of die castings. Large quantities of zinc sheet are used for the reproduction of photographic illustrations by photo-zincography.

Another very important use of zinc is in the manufacture of *brass* (page 652), in which it is alloyed with copper. Other important alloys of zinc are *german silver* and *della-metal* (page 652). It is a constituent of British silver coins minted between 1927 and 1946 (page 663).

Many zinc compounds find extensive use, e.g., the oxide, in the manufacture of paint, as a filling for rubber, and in medicine.

#### § 5 Atomic Weight of Zinc

The combining weight of zinc has been determined by the analysis of the halogen compounds, the carbonate and the sulphate, and by the synthesis of the oxide. The atomic weight is seen to be in the neighbourhood of 65 from the specific heat of zinc (0·0935); the vapour density of volatile zinc compounds and the isomorphism relationships of zinc salts.

The value recommended by the International Committee is 65·38.

#### § 6 Zinc Hydride, Oxides and Hydroxide

**Zinc hydride**,  $\text{ZnH}_2$ , is obtained by reducing zinc iodide by means of lithium aluminium hydride. It is decomposed by water with evolution of hydrogen and formation of zinc hydroxide (Wiberg, 1951).

**Zinc oxide**, *Philosopher's Wool*,  $\text{ZnO}$ , is formed when the metal is



burnt in air. Under the commercial name *zinc white*, it is manufactured by heating zinc in air and passing the fumes into condensing chambers where the powdered oxide collects.

Zinc oxide is a white powder, which appears yellow when hot and white when cold. It is almost insoluble in water, but it reacts with aqueous solutions of acids and alkalis, forming solutions of zinc salts and zincates respectively; thus behaving as an amphoteric oxide. It is reduced to the metal by carbon at a red heat, this being the method of manufacture (q.v.).

Zinc oxide is used in place of white lead (page 798) as a white pigment where white lead might undergo blackening by hydrogen sulphide. It also has the advantage of being non-poisonous. A large quantity of zinc oxide is used as a filler in the manufacture of rubber; it is also used for making glazes for certain kinds of porcelain and in medicine in *zinc ointment*.

**Zinc peroxide**,  $\text{ZnO}_2$ , is a yellowish powder made by the action of hydrogen peroxide on zinc oxide. It is decomposed by dilute acids with the formation of hydrogen peroxide.

### **Zinc Hydroxide, $\text{Zn(OH)}_2$**

Zinc hydroxide is precipitated when an equivalent quantity of an alkaline hydroxide is added to a solution of a zinc salt. It decomposes into the oxide and water when heated to  $100^\circ$ . It behaves as an amphoteric hydroxide, reacting with acids to form zinc salts and with alkalis forming zincates. The composition of the zincates formed has been variously described. In concentrated alkali solutions it is now believed that the anion present is  $[\text{Zn(OH)}_4]^-$  and that on dilution the ion present is  $[\text{Zn(OH)}_3]^-$ . These correspond to sodium salts  $\text{Na}_2\text{Zn(OH)}_4$  and  $\text{NaZn(OH)}_3$ . Zinc hydroxide also "dissolves" in aqueous ammonia, and ammonium chloride, not because of the amphoteric nature of zinc hydroxide, but on account of the formation of complex ions: behaviour reminiscent of that of copper (page 655). The solution contains probably the ion  $\text{Zn(NH}_3)_4^{2+}$ .

## **§ 7 Zinc Salts**

Zinc forms only one series of salts, and these are, in general, colourless and very soluble in water. They often crystallize with water of crystallization.

**Zinc carbonate**,  $\text{ZnCO}_3$ , occurs native as *calamine*. If sodium carbonate solution be added to a solution of a soluble zinc salt, a *basic carbonate*,  $\text{ZnCO}_3 \cdot 2\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$ , is precipitated; but the use of sodium bicarbonate results in the formation of zinc carbonate. It is a white powder, which readily decomposes on heating. It is used in medicine for the treatment of skin diseases.

**Zinc chloride**,  $\text{ZnCl}_2$ , is obtained in solution by dissolving zinc in hydrochloric acid. The concentrated solution deposits crystals of the

composition  $\text{ZnCl}_2 \cdot 2\text{H}_2\text{O}$ ; but the anhydrous salt cannot be obtained from this since hydrochloric acid is also lost and a basic chloride is formed:



The anhydrous salt is obtained by passing chlorine or hydrogen chloride over heated zinc. Industrially, it is made by heating zinc sulphide in a stream of chlorine.

It is a white, very deliquescent solid and is used as a dehydrating agent. It is very soluble in water: 100 grams of water will dissolve 330 grams of anhydrous salt at  $10^\circ$ . It combines with zinc oxide to form a hard and insoluble oxychloride; this property is applied in dentistry. It is also used (under the name of *killed spirits*) as a flux in soldering. It also combines with ammonia; e.g.,  $\text{ZnCl}_2 \cdot 6\text{NH}_3$  is formed from solid zinc chloride and ammonia at ordinary temperature. This compound is sometimes used (e.g., in organic chemistry) as a solid source of ammonia and the property of zinc chloride of combining with ammonia is sometimes likewise employed.

**Zinc sulphide**,  $\text{ZnS}$ , occurs native, and is the principal ore of zinc (page 714). It is formed as a white, amorphous precipitate when an alkaline sulphide is added to a solution of a zinc salt, or when hydrogen sulphide is passed through an alkaline solution of a zinc salt. It is not acted upon by organic acids, but reacts with mineral acids with evolution of hydrogen sulphide. Although pure zinc sulphide is not phosphorescent, it can readily be obtained in a strongly phosphorescent form. Minute traces of manganese, etc., confer on it this property. (Cf. barium sulphide, page 711.) Zinc sulphide also finds application as a white pigment.

### **Zinc Sulphate, White Vitriol, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$**

Zinc sulphate can be obtained by acting upon zinc or zinc oxide with dilute sulphuric acid. The concentrated solution deposits transparent crystals of the composition  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . The crystals are very soluble in water: 100 grams of water dissolve 96.5 grams of crystals at  $20^\circ$ . It is used in the manufacture of *lithopone*, a white pigment consisting of a mixture of zinc sulphide and barium sulphate made by the interaction of barium sulphide and zinc sulphate. This is a good paint for many purposes, although it is not suitable for outside work.

## **§ 8 Detection and Determination of Zinc**

Zinc is often detected by heating the suspected compound on charcoal with sodium carbonate. The formation of an incrustation of zinc oxide, which is yellow when hot and white when cold, is evidence of the presence of zinc. If this incrustation be moistened with a drop of cobalt nitrate solution and heated again, the formation of a green mass (Rinmann's green) indicates the presence of zinc.

Zinc is precipitated in qualitative analysis as its sulphide in *alkaline* solution. It is distinguished from other sulphides precipitated in similar conditions as it is the only white sulphide.

Zinc is conveniently determined gravimetrically by precipitating it as zinc ammonium phosphate, which on ignition is converted into the pyrophosphate. (Cf. magnesium, page 694.)

A 1 per cent solution of quinaldinic acid gives a white precipitate of  $\text{Zn}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_2 \cdot \text{H}_2\text{O}$  when added to a solution of a zinc salt faintly acid with acetic acid. Copper, cadmium, iron and chromium must first be removed, as they also give precipitates; but cobalt, nickel and manganese do not interfere. This is a very sensitive test for zinc, and can be applied also to its determination.

"Oxine" (8-hydroxy-quinoline) can also be used for the determination of zinc which is precipitated as  $\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2$  in presence of sodium (or ammonium) acetate and acetic acid.

## § 9 Cadmium, Cd

### History and Occurrence

The term *καδμεία* (*cadmeia*) was applied by Dioscorides, and by Pliny, to a zinciferous earth (calamine)—found on the shores of the Black Sea—which when melted with copper furnished brass—aurichalcum. Pliny also applied the term "cadmia" to the tutty (impure zinc oxide) found in the flues of brass-founders' furnaces. In 1817 F. Stromeyer discovered a yellow oxide free from iron in a sample of zinc carbonate used at the smelting works at Salzgitter. This could only be due to the presence of a new metal which he called "cadmium," from *cadmia fornacum*, because the metal was found in the "flowers of zinc," that is, the flue dust of the zinc furnace.

### Occurrence

This element does not occur free. It is commonly found accompanying zinc in calamine and zinc blende. Very few zinc ores contain more than 0.5 per cent of cadmium. The rare mineral *greenockite*, cadmium sulphide,  $\text{CdS}$ , is of no commercial importance.

### Extraction

The first product of the distillation of zinc ores contains most of the cadmium, partly as metal, partly as oxide. The product, called "crude cadmium," contains some zinc from which it can be separated by repeated distillation or by electrolysis. Increasing demand has also led to the development of processes for the recovery of the cadmium contained in zinc and brass "fumes" where these metals are being heated. The deposited "fume" is collected and mixed with four-fifths of its weight of fine coal and distilled at a dull red heat. By careful control of the conditions most of the zinc remains in the retort and the cadmium vapour is caught in porous refractory slabs from which it is recovered by dissolving in dilute hydrochloric acid and reprecipitation with zinc.

Cadmium is also recovered from the vat residues of the electrolytic refining of zinc by precipitation with zinc.

### Properties

Cadmium is a white metal, which melts at  $320.9^\circ$  and boils at  $766^\circ$ . It is ductile at ordinary temperatures. It is very slowly oxidized in moist air, but will burn when heated, forming brown fumes of the oxide. It resembles zinc in many of

its chemical properties, though it is usually less active. It differs from zinc principally in that its hydroxide is not amphoteric and its sulphide can be precipitated in presence of dilute acids.

#### Uses of Cadmium

Cadmium is being used in increasing quantities as a plating material, particularly in the motor-car industry; electro-plating being effected from a bath of cadmium cyanide dissolved in sodium cyanide solution. It is also used for the production of yellow pigments, in particular *cadmium lithopone*, in which cadmium sulphide replaces the zinc sulphide of ordinary lithopone (page 720), and *cadmium yellow* which consists of cadmium sulphide. A mixture of cadmium sulphide and selenide has also been used as a pigment. Cadmium is used as a constituent of fusible metals (e.g., Wood's alloy, which contains bismuth, lead, tin and cadmium in the proportions 4 : 2 : 1 : 1 and melts at 71°). Cadmium is also used in conjunction with cadmium sulphate in the Weston cadmium cell which is used as a standard of E.M.F. Cadmium (0.5 to 1.0 per cent) is alloyed with copper for overhead conductors on electric railways, and is used in some anti-friction alloys and solders.

#### Atomic Weight

The combining weight of cadmium has been determined by the conversion of the metal, and of the oxalate, to the oxide; the metal into the sulphide or sulphate; by the reduction of the carbonate to the metal, and by the precipitation of the chloride and bromide with silver nitrate. The most probable value for the atomic weight is considered by the International Committee to be 112.41.

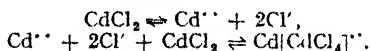
### § 10 Compounds of Cadmium

**Cadmous oxide**,  $\text{Cd}_2\text{O}$ , is obtained by dissolving cadmium in fused cadmium chloride, treating the product with water, which forms **cadmous hydroxide**,  $\text{CdOH}$ , and gently heating this. It is a yellow powder.

**Cadmium oxide**,  $\text{CdO}$ , is formed when the metal is burnt in air. It has a rich brown colour.

**Cadmium hydroxide**,  $\text{Cd}(\text{OH})_2$ , is precipitated as a white powder on addition of solutions of alkali hydroxides to a solution of a cadmium salt. Unlike zinc hydroxide, it is not attacked by excess of alkali hydroxide, but, like the zinc compound, it forms a soluble complex compound when treated with ammonia solution.

Cadmium salts are usually colourless and their solubility relations resemble those of zinc. They are notable for the low conductivity of their solutions; in this respect resembling the compounds of mercury. This behaviour is attributed to the formation of *autocomplexes*. Thus, in solutions of cadmium chloride the following equilibria are believed to exist:



**Cadmium sulphide**,  $\text{CdS}$ , occurs naturally as the rare mineral *greenockite*, and is prepared by the action of hydrogen sulphide on a solution of a cadmium salt. It varies in tint from bright yellow to orange-red, according to the temperature of precipitation, etc. If hydrogen sulphide be passed through a solution of cadmium chloride, the precipitate which forms is an intense orange-red owing to the formation of *cadmium thiochloride*:  $\text{Cl}-\text{Cd}-\text{S}-\text{Cd}-\text{Cl}$ . The thiochloride passes into the sulphide by the continued action of hydrogen sulphide and the precipitate becomes lighter in colour. It is not attacked by dilute, but does react with concentrated, mineral acids, hydrogen sulphide being liberated.

Cadmium sulphide is used as a pigment: but must not be employed in conjunction with white lead, as lead sulphide forms slowly if this is done. It is now used also in the form of *cadmiopone*, the cadmium analogue of lithopone (page 720).

**Cadmium sulphate**,  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , is made by treating cadmium oxide with dilute sulphuric acid. The concentrated solution deposits crystals of the composition shown. (Cf.  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .) It forms colourless monoclinic crystals, and is soluble in water; 100 grams of water dissolve 76.3 grams of anhydrous salt at  $15^\circ$ .

It is used in the construction of the Weston cadmium cell, which is a standard of E.M.F. This cell has a very low temperature coefficient on account of the small change in the solubility of cadmium sulphate with change of temperature.

### § 11 Detection and Determination of Cadmium

The most characteristic reaction of cadmium salts is the formation of the bright yellow precipitate of the sulphide with hydrogen sulphide. It is distinguished from arsenic sulphide, which is also yellow and precipitated in presence of dilute acid, by being insoluble in yellow ammonium sulphide with which arsenic sulphide forms a soluble compound. Cadmium is separated from other metals whose sulphides are also insoluble in dilute acids and yellow ammonium sulphide, by means of the formation of soluble complex compounds when the hydroxide is treated with ammonia solution. Copper hydroxide also forms a similar soluble complex, but cadmium can be separated from it since hydrogen sulphide precipitates cadmium sulphide from a solution of its cyanide in excess of potassium cyanide solution, whereas copper sulphide is not precipitated under these conditions (see pages 264, 660).

Cadmium can be determined electrolytically by deposition from cyanide solutions. It can also be precipitated as sulphide from slightly acid solutions; the sulphide being then converted into the sulphate by the action of sulphuric acid, and weighed as such. It can also be obtained by precipitation as the carbonate; and the formation of the double ammonium cadmium phosphate has also been employed. The latter salt, on ignition, leaves a residue of cadmium pyrophosphate ( $\text{Cd}_2\text{P}_2\text{O}_7$ ).

### § 12 Mercury, Hg. History, Occurrence and Extraction

#### History

Mercury was mentioned 300 B.C. by Theophrastus as  $\chiυρός άργυρος$  (*chylos argyros*), quicksilver or liquid silver; and he states that it can be made by rubbing vinegar with cinnabar in a copper vessel. Discorides called it  $υδωρ άργυρος$  (*hydor argyros*), liquid silver; hence the Latin *hydrargyrum*, and the present-day symbol Hg. The metal had a certain fascination for the alchemists, and for a time they believed that it, or something similar, was a constituent of all metals. "Nimble volatile mercury" was named after the mythological Mercury, the messenger of the gods, and accordingly the ancient chemists symbolized the metal by the caduceus or herald's wand ☿, also used for the planet Mercury.

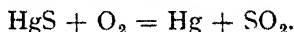
#### Occurrence

Free mercury in small quantities occurs disseminated in the ores of mercury, which in turn occur in relatively few places in payable quantities. The mercury deposits are usually found along lines of profound volcanic disturbances. *Cinnabar*,  $\text{HgS}$ , is the chief ore of mercury, and it is mined in Almaden (Spain), Idria (Carniola), Bavarian Palatinate, Peru, California, Japan, China, etc. The great quicksilver

mine at Almaden is said to have been worked at least as far back as 415 B.C. Pliny (*ca.* A.D. 77) reported that 10,000 lb. of cinnabar were brought to Rome per annum from this locality. The American deposits range from Alaska along the Pacific slope down to Peru. At one time the output from America rivalled that from Almaden, but, unlike the latter deposits, the American, and indeed most others, decrease in value with increasing depth.

### Extraction

Mercury is obtained almost exclusively from cinnabar,  $\text{HgS}$ . The ore is first crushed dry and then screened into two grades. The larger-sized pieces are sorted by hand into rich ore, poorer ore and waste. The poorer ore is mixed with that part of the original ore which passed through the screen and the whole is powdered and treated by the flotation process (page 600). The rich ore and concentrates are roasted to oxidize the sulphur, and the metal is liberated:



The reaction takes place at a temperature higher than the boiling point of mercury which therefore distils, and is condensed. Different condensing arrangements are used at different works. The mercury, for example, may be condensed in large chambers as at Idria; or in a series of pear-shaped vessels—aludels—connected in rows nearly fifty feet long, as at Almaden.

The crude mercury may be cleaned by filtration through chamouis leather; and purified by distillation from iron retorts. In the laboratory, mercury is often purified by running a fine spray of mercury down a long column of dilute nitric acid, followed by distillation *in vacuo*. For this purpose a convenient apparatus is that illustrated in Fig. 31.2.

A convenient method for cleaning mercury in the laboratory is to cover it with dilute nitric acid and aspirate a rapid current of air through the whole for some time.

### § 13 Properties of Mercury

Mercury is a silvery-white metal with a bluish tinge: it is the only pure metal which is liquid at the ordinary temperature. Its melting point is  $-38.87^\circ$ , at which temperature it forms a malleable solid. It boils at  $356.58^\circ$ . It has a slight vapour pressure, even at ordinary temperatures, and the vapour is poisonous.

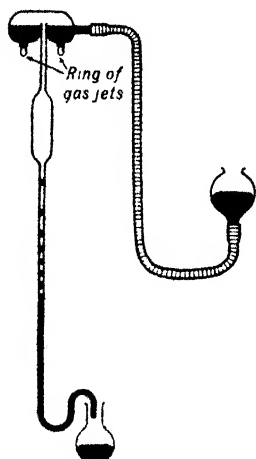


FIG. 31.2 -- Distillation of Mercury *in vacuo*

Mercury does not tarnish in the air in ordinary circumstances, but is slowly oxidized when heated to its boiling point in air or oxygen. It reacts vigorously with chlorine, and combines with iodine and with sulphur if rubbed with them in a mortar. Mercury is not attacked by hydrochloric acid; concentrated sulphuric acid acts very slowly in the cold; but when heated mercuric sulphate and sulphur dioxide are formed. Concentrated nitric acid rapidly attacks mercury, forming mercuric nitrate and oxides of nitrogen. Dilute nitric acid acts slowly, giving mercurous nitrate. Alkali hydroxides have no appreciable action on mercury.

### Amalgams

Mercury is a good solvent for some of the metals and the solutions are called amalgams. These as a rule appear to be solutions in mercury of the metal or of a compound of the metal and mercury. **Sodium amalgam** is made by pressing pieces of clean sodium under the surface of mercury: a bright flash occurs as each piece of sodium dissolves and a solid compound is formed. Gold, silver, cadmium, tin, bismuth, lead and zinc also readily form amalgams at ordinary temperatures. Finely divided copper readily amalgamates, but in mass the action is slow. Arsenic, antimony and platinum can be amalgamated with difficulty, while cobalt, nickel and iron do not amalgamate directly.

When a little sodium amalgam (containing about 1 per cent of sodium) is placed in a solution of ammonium chloride the mercury swells up into a buttery mass, thirty times its original volume, which is known as **ammonium amalgam**. Its exact nature is somewhat doubtful, but it is believed that when prepared below  $0^{\circ}$  it is a true ammonium amalgam, but that at higher temperatures it decomposes into mercury, hydrogen and ammonia.

**Silver-tin amalgam** is used as a dental filling. It is made by mixing mercury with an alloy of silver and tin of composition corresponding to  $\text{Ag}_3\text{Sn}$ . The mixture when first prepared is plastic but after a few hours it sets to a hard silver-coloured mass:



### Uses of Mercury

Mercury is widely used in physical apparatus such as thermometers, barometers, etc. It is used in the manufacture of vermilion (mercuric sulphide); considerable quantities are used for making mercury fulminate, which is extensively employed as a detonator; and a certain amount is used in medicine in the form of calomel (q.v.). Tin amalgam was formerly employed for "silvering" mirrors, and amalgams of gold, copper and zinc are used in dentistry for stopping teeth. Amalgamated zinc is used in electric batteries, because action takes place only when the circuit is closed. Sodium amalgam is used in the laboratory, in conjunction with water, as a reducing agent.

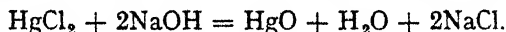
Mercury is now employed in large quantities in the mercury arc rectifiers for the conversion of alternating current to direct current, especially for direct-current electric railways (e.g. the electrified sections of the Southern Region of British Railways).

### § 14 Atomic Weight of Mercury

Several reactions have been used for the determination of the combining weight of mercury, including reduction of the oxide, chloride and bromide to the metal, and the conversion of the chloride and bromide to silver chloride and bromide. Using the last-named method, Hönigschmid obtained results leading to the value 200.61 for the atomic weight of mercury, and this is the value recommended by the International Committee. That the atomic weight lies somewhere near 200 is indicated by the specific heat of mercury (0.333), by the vapour density of volatile compounds and by the position of the element in the Periodic Table.

### § 15 Oxides of Mercury

The principal oxide of mercury is **mercuric oxide**,  $\text{HgO}$ . This appears to exist in two forms, red and yellow. Thus, if a solution of a mercuric salt be treated with excess of an alkaline hydroxide in the cold, a yellow precipitate is obtained which probably results from the immediate decomposition of the mercuric hydroxide first formed:



If the precipitation be made from hot solutions, an orange precipitate is obtained, while heating mercury in air or careful ignition of the nitrate gives a red product. The difference appears to be one of particle size only, and the yellow oxide is more active than the red, probably on account of its finer state of subdivision. Hence its use in the preparation of chlorine monoxide (page 543) and hypochlorous acid (page 546).

When heated, the yellow oxide becomes red, and the red oxide darkens in colour, finally becoming almost black, the red colour returning on cooling. If heated to a temperature somewhat above that at which blackening takes place, the oxide decomposes into mercury and oxygen. This is the way in which oxygen was discovered (page 300). Both forms of the oxide are slightly soluble in water: at 25° one litre of water dissolves 0.0513 gram of the red oxide and 0.0518 gram of the yellow. The solution has an alkaline reaction.

The action of an alkali hydroxide on a solution of a mercurous salt gives a black precipitate—the so-called **mercurous oxide**. It is, however, thought to be a mixture of mercuric oxide and mercury; in any case it always contains some free mercury.

**Mercury peroxide**,  $\text{HgO}_2$ , is formed as a red powder by the addition of hydrogen peroxide and alcoholic potash to a solution of mercuric chloride in alcohol.



### § 16 Salts of Mercury

Mercury forms two series of salts, mercurous and mercuric. In the latter the mercury is bivalent, in the former apparently univalent.

There has been some doubt as to the true nature of the mercurous compounds, but the experiments of H. B. Baker on the vapour density of very dry mercurous chloride (page 728), and of Ogg on the E.M.F. of suitable concentration cells, have shown that the mercurous compounds contain the group  $\text{—Hg—Hg—}$  so that the metal is actually bivalent.

Mercurous salts are mostly insoluble in water, the nitrate being the only important soluble one. The mercuric salts are more often soluble, the principal insoluble ones being the sulphide and iodide. The mercuric salts are remarkable for the low degree to which they are ionized in solution, as indicated by their very low conductivity. Mercuric cyanide is the extreme case, for it gives a non-conducting solution which does not give the usual "reactions" of mercuric mercury.

Mercuric salts are reduced to mercurous salts (see, e.g., page 729) and sometimes to metallic mercury. Mercurous salts are correspondingly oxidized to mercuric by oxidizing agents. Mercury is displaced from solutions of its salts, whether mercurous or mercuric, by all metals except gold and the platinum metals.

### § 17 Mercurous Salts

**Mercurous carbonate**,  $\text{Hg}_2\text{CO}_3$ , is obtained as a yellow powder by addition of sodium bicarbonate solution to a solution of mercurous nitrate. It decomposes on heating into mercuric oxide, mercury and carbon dioxide.

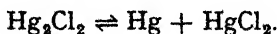
#### **Mercurous Chloride, Calomel, $\text{Hg}_2\text{Cl}_2$**

This salt can be obtained by grinding mercuric chloride with mercury and subliming the product, the sublimate being washed with water until free from mercuric chloride:



It can also be made by the direct union of mercury and chlorine; and by the addition of a soluble chloride or, better, hydrochloric acid, to a solution of a soluble mercurous salt, when mercurous chloride is precipitated.

Mercurous chloride is a white powder, almost insoluble in water: 1 litre of water dissolves only 0.0002 gram at  $18^\circ$ . It sublimes at  $373^\circ$  and its vapour density is 117.75 ( $\text{H}_2 = 1$ ) which seems to indicate a formula  $\text{HgCl}$ . This value would be equally in accord with the facts if the mercurous chloride vapour were dissociated into mercury and mercuric chloride.



H. B. Baker has claimed that the vapour density of perfectly dried calomel is 235.5, and this supports the view that the formula is  $\text{Hg}_2\text{Cl}_2$ , and that the low value of the vapour density ordinarily obtained is due to dissociation. The lowering of the freezing point of fused mercuric chloride by the addition of calomel also indicates the "double" formula.

Mercurous chloride forms a black compound with ammonia, which appears to be **mercuric amido-chloride**,  $\text{Hg}(\text{NH}_2)\text{Cl}$ , mixed with metallic mercury. The salt is also blackened by alkalis as well as ammonia, and this may be the origin of the name *calomel*—from the Greek *καλομέλας* (*kalomelas*), black. The solid also absorbs ammonia gas, forming  $\text{Hg}_2\text{Cl}_2 \cdot 2\text{NH}_3$ .

Mercurous chloride is used in medicine as a purgative, etc. For this purpose it is important that it should be free from the highly poisonous mercuric compound.

**Mercurous oxide**,  $\text{Hg}_2\text{I}_2$ , is formed when mercuric iodide or iodine is rubbed up with the right proportion of mercury, in presence of alcohol; or by addition of potassium iodide solution to a solution of a mercurous salt. It is a greenish-yellow powder slightly soluble in water, which decomposes on standing or heating into mercuric iodide and mercury.

**Mercurous nitrate**,  $\text{Hg}_2(\text{NO}_3)_2$ , is deposited in colourless monoclinic crystals of  $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  from solutions of mercury in cold dilute nitric acid, the mercury being kept in excess. This salt is soluble in water containing a little nitric acid, but excess of water decomposes it, precipitating a **basic nitrate**,  $\text{Hg}_2(\text{OH})\text{NO}_3$ . On boiling this with water, mercuric nitrate and mercury are formed. Dry mercurous nitrate, on heating, decomposes into mercuric oxide and nitrogen peroxide.

**Mercurous sulphide**,  $\text{Hg}_2\text{S}$ , is said to be formed in brownish-black plates by the prolonged action of cold, concentrated sulphuric acid on mercury, but there is some doubt as to its existence. The action of hydrogen sulphide on mercurous salts gives a mixture of mercuric sulphide and mercury.

**Mercurous sulphate**,  $\text{Hg}_2\text{SO}_4$ , is formed by warming concentrated sulphuric acid with excess of mercury, or by adding dilute sulphuric acid to a solution of mercurous nitrate. It is a white solid, very sparingly soluble in water. It is used in the Weston cadmium cell (page 722).

### § 18 Mercuric Salts

Mercuric carbonate has not been prepared, and only **basic mercuric carbonates** are known. The addition of potassium carbonate to a solution of mercuric nitrate gives a brown precipitate of  $\text{HgCO}_3 \cdot 2\text{HgO}$ ; whilst that of potassium bicarbonate gives a brown precipitate of  $\text{HgCO}_3 \cdot 3\text{HgO}$ .

**Mercuric chloride, corrosive sublimate**,  $\text{HgCl}_2$ , was formerly made,

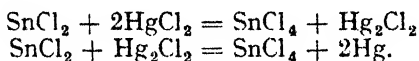
on a commercial scale, by heating a mixture of mercuric sulphate with sodium chloride, a little manganese dioxide being usually added to prevent the formation of mercurous chloride:



Mercury reacts rapidly with chlorine, especially when heated, and mercuric chloride is now being made in this way commercially.

Mercuric chloride sublimes as a white translucent mass. It is soluble in water—100 grams of water dissolve 5.6 grams at 15°—and by cooling a hot saturated solution, the salt can be obtained in needle-like rhombic prisms. It volatilizes at a comparatively low temperature: it melts at 275° and boils at 301°. It readily forms oxychlorides, e.g.,  $\text{HgCl}_2 \cdot \text{HgO}$ , and double salts like  $\text{HgCl}_2 \cdot \text{HCl}$ . The double salts, such as sodium mercuric chloride,  $\text{Na}_2\text{HgCl}_4$  (obtained by dissolving mercuric chloride in an aqueous solution of sodium chloride), are more soluble than mercuric chloride itself and they are much used in making antiseptic solutions, e.g., by taxidermists. Mercuric chloride is a valuable antiseptic, and an aqueous solution (1:1000) is used for sterilizing surgical instruments. It is a virulent poison.

When solutions of mercuric chloride are treated with reducing agents, a white precipitate of calomel results, and on occasion further reduction occurs resulting in the formation of metallic mercury. Thus, with stannous chloride:



When a solution of mercuric chloride is treated with excess of ammonia solution, a bulky white precipitate of **mercuric amidochloride** (infusible white precipitate),  $\text{NH}_2 \cdot \text{HgCl}$ , is formed. If the order of mixing be reversed, or, better, if mercuric chloride be added to a boiling solution of ammonium chloride, **mercuric diamminochloride** (fusible white precipitate),  $\text{Hg}(\text{NH}_3)_2\text{Cl}_2$ , is formed. It is called fusible white precipitate because, when heated, it fuses and then volatilizes, whereas infusible white precipitate volatilizes without fusing. The relation between the two is indicated:



**Mercuric iodide**,  $\text{HgI}_2$ , is obtained by adding potassium iodide solution to mercuric chloride, avoiding excess of potassium iodide, or by grinding mercury with the correct amount of iodine. A yellow precipitate is formed which quickly turns a brilliant scarlet.

Mercuric iodide exists in two forms, a red and a yellow. If the red form, which is tetragonal, be heated above 130°, it changes into the yellow (rhombic) form. This reverts to the red form on cooling, and scratching. Mercuric iodide melts at 259° to a red liquid, and a part sublimes forming yellow rhombic needles.

Mercuric iodide reacts with excess of potassium iodide solution,

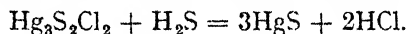
forming a solution containing potassium mercuric iodide,  $K_2HgI_4$ . This solution, made alkaline with sodium or potassium hydroxide, is known as *Nessler's Solution*. Nessler's solution is used for the detection and determination of small traces of ammonia, e.g., in water analysis. Ammonia gives a yellow or brown coloration with Nessler's Solution, the intensity of which depends upon the amount of ammonia present.

**Mercuric nitrate**,  $Hg(NO_3)_2$ , is prepared by boiling mercury with an excess of nitric acid until the solution gives no precipitate with a little sodium chloride. If evaporated over sulphuric acid, deliquescent crystals of  $2Hg(NO_3)_2 \cdot H_2O$  are formed. If the mother liquor be boiled, a compound,  $Hg(NO_3)_2 \cdot HgO \cdot 2H_2O$ , is precipitated, and if this precipitate or mercuric nitrate be treated with excess of cold water, the basic nitrate  $Hg(NO_3)_2 \cdot 2HgO \cdot H_2O$  is precipitated. Thus, like mercurous nitrate, mercuric nitrate has a great tendency to form basic salts.

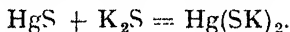
### Mercuric Sulphide, Vermilion, $HgS$

Mercuric sulphide occurs naturally as the mineral *cinnabar* which is the chief source of mercury. A black form occurs as the rare mineral, *metacinnabar*.

It is made by rubbing mercury and sulphur together in a mortar, and is also formed as a black precipitate by the action of hydrogen sulphide on a solution of a mercuric salt. When hydrogen sulphide is first passed through the solution (acidified with hydrochloric acid), a white, or pale yellow, precipitate is formed which is thought to be *mercury thioclauride*,  $Cl-Hg-S-Hg-S-Hg-Cl$ . This gradually turns brown and then black as the current of gas is continued.



The black precipitate is almost unaffected by boiling dilute acids, though hot concentrated nitric acid gradually converts it into a white *mercury thionitrate*,  $Hg_3S_2(NO_3)_2$ , and finally into mercuric nitrate. It is not attacked by solutions of ammonium sulphide or alkaline hydroxides, but concentrated solutions of alkaline sulphides, more particularly the polysulphides, convert it into solutions of thio-salts, e.g.:

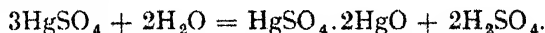


There are three different forms of crystalline mercuric sulphide. Two of these, a black form and a red form, occur in nature. Black *metacinnabar* can be prepared by treating a dilute solution of sodium mercuric chloride with excess of sodium thiosulphate. By treating a concentrated solution in the same manner, a scarlet mercuric sulphide, not cinnabar, is formed. This does not occur in nature. *Cinnabar*, the other native sulphide, is red. If the black sulphide be sublimed, a red crystalline sulphide is formed.

Mercuric sulphide is used as a pigment under the name *vermilion*, for which purpose it is made by grinding sodium sulphide with sulphur

and slowly adding mercury. It possesses the advantages of a fine colour and remarkable permanence; its cost, however, prevents its use on a large scale.

**Mercuric sulphate**,  $\text{HgSO}_4$ , is prepared by heating mercury with excess of concentrated sulphuric acid. On concentrating the solution and allowing it to cool, small silvery-white crystals of mercuric sulphate are formed. It is soluble in cold water, but it reacts with hot water, forming the basic sulphate  $\text{HgSO}_4 \cdot 2\text{HgO}$ , used in pharmacy under the name of *turpeth mineral*.



**Mercuric cyanide**,  $\text{Hg}(\text{CN})_2$ , is made by dissolving yellow mercuric oxide in aqueous hydrocyanic acid. It is used in the preparation of cyanogen (page 408) and is noteworthy in that its solutions are non-conducting (and hence, according to the ionic theory, non-ionized) and do not give the "reactions" of mercury.

**Mercuric thiocyanate**,  $\text{Hg}(\text{CNS})_2$ , made by adding mercuric chloride to a solution of potassium thiocyanate, is an insoluble white powder which when dried and ignited forms a voluminous ash. Pellets made from the dry powder, when ignited, form long snake-like tubes of ash—the so-called *Pharaoh's serpents*.

### § 19 Detection and Determination of Mercury

Mercury is usually detected by obtaining the separation of the metal. This can be done by warming copper foil with a solution of a mercury salt, when the mercury is deposited on the copper as a grey layer which becomes bright when rubbed, and may be vaporized to condense in globules on the sides of a small test-tube. Similarly, mercury compounds when heated with sodium carbonate yield the metal.

Mercury can also be determined similarly, the experiment being carried out in a crucible covered by a weighed, water-cooled silver plate, on which the mercury collects. It is, however, usually determined as mercuric sulphide.

### § 20 Relationships of the Elements of Group II

The elements of Group II are somewhat similar to those of Group I in the marked electropositive character of those in the A sub-group, and in the rather slight relationship between the members of the two sub-groups. Both these characteristics are, however, less noticeable in Group II than in Group I. Also the first two (or "typical") elements are not so clearly related to the A sub-group as in Group I and, as mentioned at the beginning of Chapter 30, they have been classified in both ways. These conclusions are supported by the electronic configurations of these elements which are shown in Tables XLIII and XLIV.

In both sub-groups there are two electrons in the outermost quantum shell, but whereas in the Alkaline Earths the removal of these two electrons leaves a system with the very stable Inert Gas structure, the loss of two electrons from an atom of zinc, cadmium or mercury exposes

a shell of 18 electrons. In the former case, as in the Alkali Metals, the 8-electron group of the penultimate shell screens the positive nucleus sufficiently to enable the two outermost electrons to be readily removed, so forming a divalent cation. It appears that the second of these electrons is more readily removed than the first so that the valency of the ions of these metals is always two. Similarly the Inert Gas structure of these ions ensures that these elements never exhibit a valency greater than two.

TABLE XLIII

Element	Number of electrons in orbit															
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p	7s
Beryllium	2	2														
Magnesium	2	2	6	2												
Calcium	2	2	6	2	6		2									
Strontium	2	2	6	2	6	10	2	6			2					
Barium	2	2	6	2	6	10	6	6	10		2	6		2		
Radium	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	2

TABLE XLIV

Element	Number of electrons in orbit														
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p
Zinc	2	2	6	2	6	10	2								
Cadmium	2	2	6	2	6	10	2	6	10		2				
Mercury	2	2	6	2	6	10	2	6	10	14	2	6	10	2	

The readiness with which two electrons are lost by atoms of the Alkaline Earth elements is indicated by the values of their electrode potentials which are higher than those of any other elements except the Alkali Metals; their reactivity is thus also second only to that of the Alkali Metals.

The two electrons in the outermost shells of zinc, cadmium and mercury might be expected to show some analogy to those of helium and be inert. This effect is not observed in zinc and cadmium but there are indications of it in mercury. Thus mercury is surprisingly volatile, its vapour is monatomic and it has a considerable tendency to form covalent, rather than electrovalent, compounds.

The loss of two electrons from the atoms of the B sub-group elements gives rise to divalent cations as in the A sub-group but, since it seems that the 18 electrons of the penultimate shell have here a lesser screening effect than the 8-electron shell of the Alkaline Earth elements, the tendency to form ions is much smaller. This is indicated by the values of their electrode potentials and electronegativities. The 18-electron shell in these elements is comparatively stable (possibly because of the greater positive charge on the nucleus) so that, by contrast with copper,

for example, there is no tendency to variable valency. As in the Alkaline Earths no valency other than 2 is observed in the soluble compounds, the mercurous compounds being only an apparent exception (see page 727).

The A sub-group includes a very well-marked triad of elements, which closely resemble each other; along with them should be included radium, which, so far as its chemical properties are known, is very similar to barium. Zinc, cadmium and mercury are also a fairly closely related triad although mercury differs substantially, in many ways, from zinc and cadmium which are very much more closely related.

The hydroxides of calcium, barium and strontium are soluble, or slightly soluble, in water; those of zinc, cadmium and mercury are insoluble. Similarly those of magnesium and the A sub-group are strongly basic, whereas the remainder are only feeble bases and may develop feeble acidic properties. The B sub-group elements also differ from the others in that their compounds are more easily reduced to the metal; they are all stable in air; their sulphides are stable and insoluble, whereas the others are decomposed by water; and the hydroxides are more easily decomposed by heat.

Beryllium, the lightest element of the group, shows many resemblances to aluminium, and mercury, which in many respects is a highly individual element, is like copper in some ways, as, for example, in the number of complex compounds it forms with ammonia. Beryllium and magnesium resemble each other quite closely, though the former is sometimes more like zinc in its behaviour than magnesium, which is more like calcium. Magnesium also shows some resemblance to lithium (cf. Chapters 28 and 29).

## CHAPTER 32

# BORON, ALUMINIUM, GALLIUM, INDIUM AND THALLIUM

### § 1 Group III of the Periodic Table

THE third group of the Periodic Table comprises the elements boron and aluminium (the members of the short periods) together with scandium, yttrium, lanthanum, the rare earths (or lanthanons), actinium, and the trans-uranium elements on the one hand; and gallium, indium and thallium on the other. Boron and aluminium are the only common elements in the group.

As in the case of Group II, there has been considerable discussion as to whether boron and aluminium are to be considered as primarily related to scandium, yttrium, etc., or to gallium, indium and thallium; but the view is now generally held that the close association of boron and aluminium with gallium, indium and thallium is, on the whole, the best arrangement. This point will be referred to again in § 1 of Chapter 33.

### § 2 Boron, B

#### History

Although mentioned in the early Latin writings on chemistry, it is probable that the term "borax" did not always refer to the substance now called "borax," since the Arabians applied the term *buraq* (borax) to many substances used as fluxes. In 1702 W. Homberg made boric acid from borax, and called the acid *sal sedativum*; H. J. Pott (1741) showed that ordinary Glauber's salt was produced at the same time. Hence, sulphuric acid and borax yield boric acid and Glauber's salt. Baron, 1748, showed that borax is a compound of Homberg's sal sedativum and soda. After Lavoisier's work on acids, the term "boracic acid" was substituted for "sal sedativum," and "boracic acid" was later abbreviated to "boric acid." J. L. Gay-Lussac and J. Thénard isolated the element in a more or less impure condition in 1808.

#### Occurrence

Boron does not occur free in nature, but it occurs as *boric acid* (also called *Tuscany boric acid*)—and as borates including *borax* and *tincal* ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and *kernite* ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ ). It is also found in the form of complex borates, notably *colemanite* ( $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ ), in Asia Minor and America; *boronatrocaltite* ( $\text{CaB}_4\text{O}_7 \cdot \text{NaBO}_2 \cdot 8\text{H}_2\text{O}$ )



in Chile, and *boracite* ( $2\text{Mg}_3\text{B}_8\text{O}_{15} \cdot \text{MgCl}_2$ ) at Stassfurt. Boric oxide has been reported in sea-water, and it has been found in small quantities in soils, in most vegetable products, in plant ashes and in some wines. It is not usually present in animal products.

### Extraction of Boron

The element boron is very difficult to obtain in a really pure condition. It has usually been obtained by heating the oxide with sodium, potassium, magnesium or aluminium in a covered crucible:



The fused mass is boiled with dilute hydrochloric acid, and a dark brown powder of **amorphous boron** remains. Boron has been obtained by the electrolysis of a mixture of boric oxide with magnesium oxide and fluoride at  $1100^\circ$ , using a carbon crucible as anode and an iron cathode. The magnesium liberated at the cathode reduces the borate to boron which is deposited on the cathode, and yields amorphous boron on treatment with hydrochloric acid. (Andrieux, 1929.)

**Crystalline boron** has been made by dissolving boron in molten aluminium at a high temperature. The solution, on cooling, deposits crystals of boron which can be obtained by removing the aluminium by boiling with sodium hydroxide. Some think that this crystalline boron is really an alloy or a compound of boron and aluminium since it always persistently retains aluminium and carbon. A crystalline boron, said to be of 99 per cent purity, has been made by striking an alternating-current arc between water-cooled copper electrodes in a globe containing a mixture of boron trichloride and hydrogen; it can also be got by passing a mixture of boron trichloride, or tribromide, mixed with hydrogen over an electrically heated tantalum filament. The success of this method depends upon the fact that the halogen compounds are decomposed at a temperature much below that at which boron and tantalum combine.

### Properties

Amorphous boron is a brown powder of specific gravity 1.73. The purest crystalline boron so far obtained is very hard, and has a quasi-metallic lustre, and a sp. gr. 2.33. Boron melts at about  $2100^\circ$  and boils at  $2550^\circ$ .

Boron burns to the trioxide ( $\text{B}_2\text{O}_3$ ) brilliantly when heated in oxygen, and also burns in air, forming a mixture of oxide and nitride (BN). Oxidizing agents (e.g., nitric acid) oxidize boron to boric acid; boron also reacts with fused alkali hydroxides, forming borates, with the evolution of hydrogen.

Crystalline boron is relatively inert; it burns only very slowly in air even at a very high temperature, and unless in a finely divided condition it is not attacked by concentrated nitric or sulphuric acids.

Until recent times boron itself had not found any applications, but it is now used, like calcium boride, as a deoxidizer for metals. Borax and boric acid (q.v.) are also important technically and a number of metallic borides (e.g., chromium, molybdenum and tungsten) seem likely to have applications in gas turbines and similar spheres where hardness, high melting point and resistance to corrosion are required.

### Atomic Weight of Boron

The vapour densities of volatile compounds of boron, such as the chlorides, and volatile organic compounds, indicate a value for the atomic weight of boron in the neighbourhood of 11. Dulong and Petit's rule gives results which do not agree with this value, but the position of boron in the Periodic system supports the value 11. The exact value has proved difficult to determine with accuracy. It has been attempted by determining the weight of water in a given weight of borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and by conversion of the halides into silver halides. The latest value (1957) recommended by the International Committee is 10.82, based on the determination by Honigschmid by the last-named method.

### § 3 Compounds of Boron

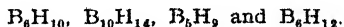
The compounds of boron exhibit, in general, the properties of the compounds of a non-metal. They indicate that the element is trivalent. The hydrides (e.g.,  $\text{B}_2\text{H}_6$ ) seem to indicate the possibility of quadrivalency, but this is probably an incorrect deduction from their formula, though the question is still not definitely settled (see below).

#### Boron Hydrides

The existence of a hydride of boron was first reported by Sir H. Davy in 1810. F. Jones in 1879 investigated the product of the action of dilute acids on magnesium boride (made by strongly heating boron trioxide with magnesium powder), and this reaction was also examined by Ramsay and Hatfield in 1901. Magnesium boride is usually formulated as  $\text{Mg}_3\text{B}_2$  but it is now believed to be  $\text{MgB}_2$ . The systematic investigation of the hydrides of boron is due to Stock and his co-workers (1912 onwards).

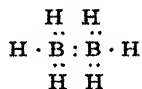
Stock passed the gases evolved when magnesium boride is dropped into dilute hydrochloric acid through a vessel immersed in liquid air, thus condensing them to a white solid which is a mixture of boron hydrides with silicon hydride, carbon dioxide, and other impurities.

Stock showed that the chief product is a hydride  $\text{B}_4\text{H}_{10}$  which soon breaks up into another,  $\text{B}_2\text{H}_6$ , and hydrogen. Other hydrides isolated by him were shown to have the formulae:

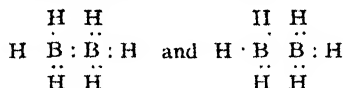


The assignment of constitutional formulae to these compounds presents some difficulty. At first sight, their molecular formulae seem to suggest that in them boron might be quadrivalent like carbon but the position of boron in the Periodic Table and the formulae of its other compounds renders this improbable. A suggestion which gained a good deal of support at one time was that in, for example,

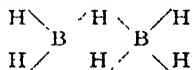
$B_2H_4$ , two of the hydrogen atoms were attached by single-electron links (cf. page 832) leading to the electronic formula:



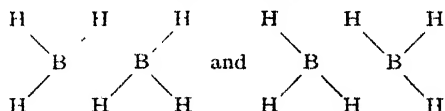
This view is supported by the great instability of these compounds which very readily lose hydrogen; but this leaves each boron atom with only seven electrons in the outermost ring. This idea requires modification in view of the development of the theory of resonance, since measurements of the bond lengths indicate that they are all longer than ordinary single covalencies. This would involve resonance between structures such as the one given above and



Longuet-Higgins and Bell (1943) postulated the existence of resonance bridges between some of the boron atoms. They represent  $B_2H_6$ , for example, as



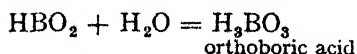
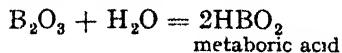
where the terminal B-H bonds are normal covalencies and the central bonds (shown dotted) are the result of resonance between structures such as



The existence of the hydrogen bridge in which the two hydrogen atoms concerned lie, respectively, above and below the plane in which the two boron and four hydrogen atoms all lie, has now been confirmed by physical measurements, such as electron diffraction and infra-red spectrographic investigations, but the precise way in which the bridging hydrogen atoms unite the boron atoms is still in doubt. Compounds such as the boron hydrides in which there are too few electrons to furnish ordinary covalent links of paired electrons are said to be **electron deficient**. Other electron-deficient compounds are known, such as  $(CH_3)_3Al$ ,  $Al(CH_3)_3$ .

The use of a hydride (or hydrides) of boron as a rocket propellant has been reported; these compounds seem likely, therefore, to acquire a practical importance in addition to the interest of their chemical constitution.

**Boron trioxide, boric oxide,  $B_2O_3$ ,** is formed when boron is burned in oxygen, but it is usually prepared by heating boric acid to redness. The fused mass so formed solidifies to a colourless transparent glass, which has no definite melting point. When exposed to the atmosphere, boron trioxide absorbs moisture with which it combines, becoming opaque and finally passing into boric acid:

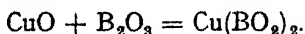


Boron trioxide is almost non-volatile, even at a red heat, and consequently it can decompose the compounds of much stronger acids, such as sulphuric acid, when heated with them to very high temperatures:



This behaviour is analogous to that of the preparation of hydrochloric acid from sodium chloride and sulphuric acid (which is a weaker acid than hydrochloric (page 537). (Cf. also the electric furnace method of making phosphorus, page 812.)

Boron trioxide is mainly an acidic oxide; but it also exhibits very feeble basic properties. With water it forms boric acid and with basic oxides it forms borates, e.g.:



The existence of unstable compounds, like the *acid sulphate*,  $\text{B}(\text{HSO}_4)_3$ , and the *phosphate*  $\text{BPO}_4$ , is evidence of its basic properties. Most of the salts, however, of either kind are largely hydrolysed by water.

#### § 4 The Boric Acids

Several boric acids are known (at least in the form of salts), all derived from boron trioxide with varying amounts of water—thus:

Orthoboric acid	$\text{H}_3\text{BO}_3$ or $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Metaboric acid	$\text{HBO}_2$ or $\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Pyroboric acid	$\text{H}_2\text{B}_4\text{O}_9$ or $2\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
Tetraboric acid	$\text{H}_2\text{B}_4\text{O}_7$ or $2\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$

Salts also exist corresponding to more complex, condensed boric acids, e.g.,  $\text{H}_4\text{B}_6\text{O}_{11}$  and  $\text{H}_2\text{B}_{10}\text{O}_{16}$ . Of the free acids, orthoboric is the only important one; of salts *borax*, the most important boron compound, is sodium tetraborate.

#### Orthoboric Acid, $\text{H}_3\text{BO}_3$

Volcanic jets of steam (soffioni) at a temperature between  $90^\circ$  and  $120^\circ$ , issuing from the fumaroles on the so-called Maremma di Toscana—or Tuscany Marshes—carry small quantities of boric acid. The steam condenses in lagoons (lagoni) of water which often surround the jets. The water of the lagoons becomes highly charged with the acid, and the boric acid can be obtained in a crystalline condition by evaporating the water of the lagoons. Artificial lagoons for arresting the jets of steam were established in Tuscany in 1818; and artificial soffioni were bored in 1854. The natural heat of the steam is utilized in concentrating the water.

A large proportion of the world's supply of boric acid is now made from the naturally occurring deposits of calcium borates in California and South America, e.g., colemanite. The mineral is powdered, mixed with boiling water, and sulphur dioxide is passed through the mixture,

whereby boric acid and calcium sulphite are formed. On cooling, the boric acid crystallizes out:



Orthoboric acid crystallizes on cooling hot aqueous solutions as white, shining plates belonging to the triclinic system. It is appreciably volatile in steam (hence its presence in the soffioni), and is sparingly soluble in cold water and reasonably soluble in hot: 100 grams of water dissolve 4 grams of  $\text{H}_3\text{BO}_3$  at  $18^\circ$  and 39 grams at  $100^\circ$ .

On heating, orthoboric acid loses water: at a temperature of  $100^\circ$ , or a little above, metaboric acid is formed:



while at about  $160^\circ$  tetraboric acid, sometimes (wrongly) called pyroboric acid, results:



When heated to a still higher temperature, it swells to a frothy mass and, finally, forms a glass of boron trioxide.

Boric acid is a very weak acid: in aqueous solution it colours litmus claret-red, and moist yellow turmeric paper is coloured brown, but, unlike the brown colour produced by alkalis, the brown stain is not destroyed by acids.

Boric acid is used in medicine as an antiseptic, and large quantities have been employed as a food preservative. Its use, however, for this purpose is now prohibited in many countries: in this country food preservatives as a whole are forbidden.

Boric acid is also used in the manufacture of glazes, particularly for enamels to be used on metals since borate glazes have a higher coefficient of expansion than silicate glazes.

**Metaboric acid**,  $\text{HBO}_2$ , is formed when orthoboric acid is heated to just over  $100^\circ$ . When dissolved in water it re-forms the ortho-acid.

## § 5 Sodium Borates. Borax

### Sodium Tetraborate, Borax, $\text{Na}_2\text{B}_4\text{O}_7$

Borax occurs naturally as *tincal* in the dried-up inland lakes of some parts of India, Tibet and California. Native tincal contains about 55 per cent of borax proper, i.e., of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . This is extracted by lixiviating the mass with water and evaporating until crystals separate.

Large quantities of borax were at one time made from native calcium borate. The powdered mineral was boiled in drums with a slight excess of aqueous sodium carbonate. Calcium carbonate is precipitated as a mud, and from the clear solution crystals of borax are obtained.

Sodium metaborate remains in the mother liquor and is converted into borax by blowing carbon dioxide through it.

Since 1926 when kernite (rasorite) was discovered it has been almost the sole source of borax. It is first extracted with hot water, which dissolves the borax; any silica in solution is precipitated and the hot filtrate, after dilution, treated with an oxidizing agent to destroy colouring matter. After further filtration the borax is obtained by crystallization.

Borax is ordinarily obtained in the form of large colourless crystals of the decahydrate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . It is sparingly soluble in cold water, but is more soluble in hot: 100 grams of water dissolve 3 grams of decahydrate at  $10^\circ$  and 99.3 grams at  $100^\circ$ . If a saturated solution be allowed to crystallize above about  $62^\circ$ , octahedral crystals of the pentahydrate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  separate; if the temperature be below  $62^\circ$ , the decahydrate is formed.

Solutions of borax are alkaline, for, since boric acid is a very weak acid, considerable hydrolysis occurs. Borax solutions can be titrated with standard hydrochloric acid using methyl orange (which is unaffected by boric acid) as indicator. (Compare similar use of sodium carbonate, page 623.)

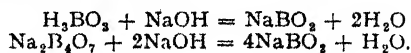
When heated, borax fuses, loses water, and swells up into a white porous mass, owing to the expulsion of the water. Finally the borax melts to a clear glass—borax glass—which is anhydrous borax. Like boric acid, fused borax dissolves many colouring oxides, giving glasses with a characteristic colour. Borax "beads" fused in a loop of platinum wire are used as tests for oxides which dissolve in the bead, and show characteristic colours as indicated in Table XLV. Thus:

TABLE XLV.—COLOURS OF BORAX BEADS WITH SOME METALLIC OXIDES

Metallic oxide	Oxidizing flame	Reducing flame
Copper . . . .	Green (hot); blue (cold)	Colourless or red
Cobalt . . . .	Blue (hot or cold)	Blue
Chromium . . . .	Green or red (hot or cold)	Green
Iron . . . . .	Yellow (cold), brown (hot)	Dirty green or olive
Nickel . . . . .	Violet (hot), brown (cold)	Grey and opaque
Manganese . . . .	Amethyst (hot or cold)	Grey and opaque

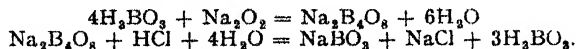
Large quantities of borax are used in the manufacture of enamels, glazes and of optical glass; in the manufacture of soap and of drying oils; for stiffening candle wicks; as a cleansing and stiffening agent in laundry work, and for glazing paper, playing-cards, etc.; in making varnishes for metals; with casein, as a substitute for gum arabic; and as a flux in soldering and brazing. It is also employed as an antiseptic.

**Sodium metaborate**,  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , can be obtained by the action of caustic soda solution on boric acid or borax.



It crystallizes in colourless needles.

**Sodium perborate**,  $\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$ , is obtained when a mixed solution of borax and sodium hydroxide is electrolysed, or treated with hydrogen peroxide. It has also been made by acting upon boric acid suspended in cold water, with sodium peroxide, and treating the salt which crystallizes out on cooling with the correct amount of a dilute acid:



Sodium perborate has strong oxidizing properties and is used as a cleansing and bleaching agent

### § 6 Other Boron Compounds

Boron combines directly with most metals and with carbon at the temperature of the electric furnace. Many of these compounds are very hard and **carbon boride**,  $\text{CB}_4$ , is possibly the hardest substance known (but see boron nitride, below).

**Boron nitride**, BN, is a white powder formed when boron is burnt in nitrogen, or heated in ammonia. It is decomposed by steam, forming boric acid and ammonia, and the occurrence of both these substances in the vapours of the solfonti of Tuscany has led to the suggestion that they are there derived from the action of steam on subterranean boron nitride.

Boron nitride has recently (1957) been converted into another crystalline form (by the application of very high pressure and high temperature) which is reported to be harder than diamond.

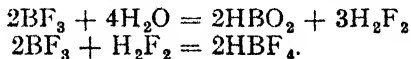
**Boron sulphide**,  $\text{B}_2\text{S}_3$ , is obtained in white needles by direct union of the elements. **Boron pentasulphide**,  $\text{B}_2\text{S}_5$ , is also known. It is decomposed by water, the vigorous reaction yielding hydrogen sulphide and boric acid.

All four halogens unite with boron to form trihalides. Of these the trifluoride and trichloride are the most important.

**Boron trifluoride**,  $\text{BF}_3$ , is a colourless, fuming gas which is best prepared by heating a mixture of concentrated sulphuric acid, ammonium fluoborate and boron trioxide:



It is manufactured by the action of hydrogen fluoride on borax followed by decomposition of the intermediate compound, first formed, with fuming sulphuric acid. It reacts vigorously with water, forming metaboric and hydrofluoric acids; the hydrogen fluoride so formed unites with unchanged boron trifluoride to form **fluoboric acid**,  $\text{HBF}_4$ :

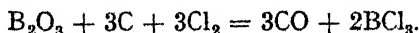


It has become important in organic chemistry on account of its remarkable catalytic activity.

**Ammonium fluoborate**,  $\text{NH}_4\text{BF}_4$ , is obtained by heating ammonium fluoride with boric acid or by neutralizing fluoboric acid with ammonia. **Potassium fluoborate** is obtained similarly from fluoboric acid and potassium hydroxide or carbonate.

**Boron trichloride**,  $\text{BCl}_3$ , is a volatile, colourless, fuming liquid

obtained by direct union of the elements; by heating an intimate mixture of boron trioxide and charcoal in a current of chlorine:



It boils at  $12.5^\circ$  and is decomposed by water into boric and hydrochloric acids. Like boron trifluoride it is used as a catalyst in organic chemistry.

### § 7 Detection and Determination of Boron

Boron usually occurs as boric acid or a borate, and if in some other state of combination may be converted into one of these by means of hot concentrated nitric acid. These are then detected by heating with sulphuric acid and a little alcohol. On setting light to the alcohol, a green-edged flame, caused by the formation of ethyl borate, indicates the presence of boron. Alternatively, the following procedure may be adopted. The suspected borate is mixed with powdered calcium fluoride and made into a paste with concentrated sulphuric acid. A platinum wire is dipped into the paste and held near to, but not in, a bunsen flame. If boron be present the flame is coloured green owing to the formation of boron trifluoride. Barium and copper, if present, do not colour the flame under these conditions.

Boron in the form of borax can be determined by titration with a mineral acid (such as hydrochloric acid), using methyl-orange as indicator. Boric acid itself can be titrated with caustic soda solution, provided a considerable proportion of mannitol or glycerol is also present in the solution. This is because boric acid readily combines with these substances to form compounds which are relatively strong acids.

### § 8 Aluminium, Al

#### History

The word "alumen," or its Greek equivalent, was formerly applied as a *grouping term* for substances with an astringent taste. Geber and some others classed alum with the "vitriols," but Paracelsus considered it to be radically different, for he pointed out that its "corpus" is not metallic but an intimate mixture of earths. The earthy "corpus" was confused with lime until J. H. Pott, 1746, showed that the base is really an argillaceous earth; and in 1754, A. S. Marggraf proved clearly that the base is entirely different from lime, and that clay contains the "alum earth" united with silica.

#### Occurrence

Aluminium (also called in the U.S.A. aluminum) does not occur free in nature, but its compounds are numerous and widely distributed. In abundance, it comes third, after oxygen and silicon.

*Corundum*, *ruby*, and *sapphire* are more or less impure forms of the oxide,  $\text{Al}_2\text{O}_3$ ; *emery* is a mixture of iron oxide and corundum. There



are three recognized hydrates occurring in nature—*gibbsite* or *hydrargillite*,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , or  $\text{Al}(\text{OH})_3$ ; *bauxite*,  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , or  $\text{Al}_2\text{O}(\text{OH})_4$ , and *diaspore*,  $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , or  $\text{AlO}(\text{OH})$ . The word **bauxite** is used in rather a general way for native aluminium hydroxides containing the equivalent of, say, 50 to 70 per cent of  $\text{Al}_2\text{O}_3$ , about 25 to 30 per cent of water, with varying amounts of ferric oxide, titanic oxide, and silica. Some bauxites approximate to the trihydrate; others appear to be mixtures of the trihydrate and lower hydrates, and some are considered to be more or less impure monohydrate. The bauxites are often classed as ferruginous, and non-ferruginous. The double fluoride—*cryolite*,  $\text{AlF}_3 \cdot 3\text{NaF}$ —is used in the manufacture of aluminium; *turquoise* is a hydrated phosphate. The *felspars* and *clays*, as well as a great number of common minerals, are complex silicates of aluminium with other bases. Bauxite and cryolite are the chief compounds used in the preparation of the metal aluminium. Artificial cryolite, free from silica, is now manufactured for this purpose.

### Isolation of the Metal

Aluminium was first isolated by F. Wohler in 1827 by warming the anhydrous chloride with potassium, as a light grey metallic powder, but it was not until 1845 that the compact metal was obtained. Deville replaced the potassium by sodium and this, until 1886, was the only method available, so that metallic aluminium until then was little more than a chemical curiosity.

The cheap production of aluminium was made possible by the discovery, by C. M. Hall in 1886, that a solution of alumina in a molten mixture of cryolite and some other fusible fluoride is an electrolyte, and that when electrolysed, aluminium collects at the cathode. Aluminium is now made entirely by electrolysis, but the process can be carried on only where electricity is cheap (e.g., where water-power is available).

The raw material is bauxite which is usually too impure to be used without a preliminary purification to remove iron, titanium and silicon oxides, which would seriously contaminate the metallic aluminium. The bauxite is roasted at a low temperature to convert the ferrous oxide into ferric oxide and then digested with a solution of sodium hydroxide under pressure which dissolves the alumina, partly as sodium aluminate and partly as a colloidal solution:



The ferric oxide, silica, etc., do not dissolve and are filtered off.

Aluminium hydroxide is then reprecipitated from the solution by agitation with a little freshly precipitated aluminium hydroxide from a previous operation, when the aluminium hydroxide gradually separates on account of the hydrolysis of the sodium aluminate in presence of "seeding" crystals, until the ratio  $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O}$  is about 1 : 6. The hydroxide is then washed, dried and ignited.

The chemistry of this operation is still uncertain. It may be that,

since alumina is a very weak acid and the sodium aluminate will therefore be considerably hydrolysed, it is present as a supersaturated solution which is "seeded" by the added aluminium hydroxide. It is possible that it may be present in colloidal solution and that the addition of freshly precipitated aluminium hydroxide provides nuclei for growth. Again, it is possible that the "seeding" brings about a polymorphic change from a less stable (and therefore more soluble) form to a more stable form of the aluminium hydroxide.

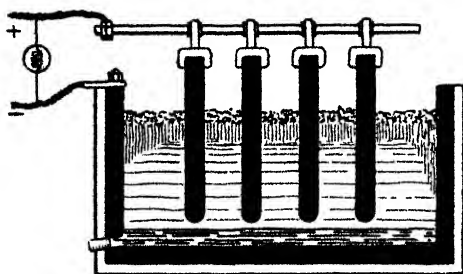


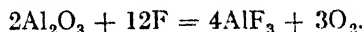
FIG 32.1.—Manufacture of Aluminium

The purified oxide is then added to a molten mixture of cryolite and fluorspar, contained in a large electrolytic cell (Fig. 32.1). This consists of an iron box about eight feet long and six feet wide lined with blocks of carbon and serves as the cathode. The anodes are a set of carbon rods.

The exact nature of the action which takes place is not certain. The following is thought to be probable. The aluminium fluoride (from cryolite) ionizes:



The aluminium is discharged at the cathode, while at the anode the fluorine reacts with the alumina re-forming aluminium fluoride, and oxygen which is liberated:



The resistance of the electrolyte to the current gives enough heat to keep the mass fluid. The liquid metal sinks to the bottom of the cell, whence it is "tapped" from time to time. The oxygen evolved at the anode either escapes as a gas or unites with the carbon of the anodes to form carbon monoxide, which either burns or escapes. Fresh supplies of bauxite are added when required.

Clays contain from 20 to 36 per cent of alumina but, until recently, no method was known for separating silica from alumina cheaply enough for manufacturing purposes. A method has been described using kaolin (china clay) as raw material but so far without commercial success as it is more expensive than the method starting with bauxite.

## § 9 Properties of Aluminium

Aluminium is a bluish-white metal capable of taking a high polish. The dull surface usually seen on the metal is an effect of a superficial film of oxide. Aluminium is lighter than most metals, its specific gravity

is 2.7 at 20°, and therefore it has nearly the same specific gravity as glass, and one-third the specific gravity of iron. The metal is ductile and malleable and can be rolled into sheets, wire, and foil. Aluminium has a tensile strength of only 4 tons to the square inch but the addition of only small amounts of other metals raises this to 25 or 30 tons. It is a good conductor of heat and electricity. Aluminium melts at 660.1°; and boils at 2330°.

Aluminium remains practically unaltered in dry air, while in moist air and in boiling water a superficial film of oxide protects the metal from further action. Even at 700° to 800° it oxidizes but slowly; at higher temperatures it burns brilliantly with the evolution of much heat. It burns readily in oxygen giving an intense white light. This property is made use of in flashlight photography. Aluminium foil contained in a bulb of oxygen at low pressure is ignited by passing a current through a low-voltage filament in contact with it.

Aluminium, when heated with the halogens and with nitrogen, forms halides and nitride respectively. Aluminium dissolves slowly in cold dilute hydrochloric acid, and rapidly in hot, the concentrated acid giving an aqueous solution of aluminium chloride and hydrogen gas. Nitric acid, dilute or concentrated, acts so slowly that nitric acid is usually said to have "no action on aluminium" and, in the U.S.A., aluminium containers have been used for transporting nitric acid. Dilute sulphuric acid has very little action in the cold, but the hot concentrated acid converts it into aluminium sulphate with the evolution of sulphur dioxide. Aluminium is rapidly dissolved by sodium and potassium hydroxides with the evolution of hydrogen and the formation of the alkali aluminate. Organic acids (e.g., acetic acid) are almost without action on the metal at ordinary temperatures, but they are said to have an appreciable solvent action in the presence of sodium chloride. Salt solutions, e.g., sea-water, rapidly corrode the metal.

Aluminium is a very intensely electropositive element (cf. Table XIX, page 231) and, in consequence, it is a powerful reducing agent. Thus, carbon monoxide and dioxide are reduced to carbon. Also, aluminium powder, when intimately mixed with many metallic sulphides or oxides, e.g., manganese, chromium, tungsten, uranium, iron, along with some flux, say, fluorspar, and ignited, reduces the oxides or sulphides to the metal; e.g., with pyrites, it forms aluminium sulphide and metallic iron. The mixture becomes very hot during the reaction and a temperature of 3000°-3500° is sometimes attained. The heat of this reaction can be utilized for softening and welding iron rails, steel castings, etc., when an intense local heat is needed. The rails to be welded are packed in a mixture of iron oxide and aluminium powder together with a special cement to make the mass compact. When the mass is ignited, it burns and heats the rails to a temperature high enough to weld the metals together. The mixture of aluminium powder with various metallic oxides is sold as "thermite," and the process is called H. Goldschmidt's or the aluminothermic process.

### § 10 Uses of Aluminium

Large quantities of aluminium powder mixed with oil are used as paint for steam-pipes and other metal objects. It is used for steam-pipes since the bright surface minimizes loss of heat by radiation, and for oil and petrol tanks to lessen absorption of heat. Aluminium is used for cooking utensils; precision instruments; surgical instruments; and as an ornamental metal for interior decoration; and artistic objects, trinkets, etc. The wire is used as a conductor of electricity in power lines because aluminium wire, though thicker than copper for a given conductivity, is not so heavy and does not strain the supports so much. Aluminium is used as a reducing agent in the production of certain metals, e.g., chromium, and in "thermite." The formation of oxides during the melting of many metals is prevented if a little aluminium be present, hence aluminium—0.16 to 0.05 per cent—is commonly added to molten steel as it comes from the Siemens-Martin or Bessemer furnace. This enables castings to be made more free from "blow holes."

Aluminium forms many useful alloys, which are finding more and more applications. Examples of some of these and their approximate compositions are given in Table XLVI.

TABLE XLVI.—ALUMINIUM ALLOYS

Alloy	Composition (per cent)						
	Silicon	Copper	Mag- nesium	Man- ganese	Nickel	Other elements	Alumin- ium
4S . . .			1	1.25			97.75
2L8 . . .		12				Zn 13	75
Alpax . . .	14						86
Y alloy . . .	0.7	4	1.5		2	Fe 0.6	91.2
RR 53 . . .	2	2.25	1.6		1.3	Fe 1.4	91.45
Duralumin . . .	0.4	4	0.6	0.6			94.4
Birmabright . . .			3-4				96-97
DTD 298 . . .		4-4.6					95.4-96

Many aluminium alloys can be hardened and strengthened by *ageing*. This phenomenon was formerly thought to be peculiar to aluminium alloys but is now known with many others.

Aluminium amalgam, made by adding aluminium filings to a 0.5 per cent solution of mercuric chloride for a couple of minutes, is a valuable neutral reducing agent.

### § 11 Atomic Weight of Aluminium

The vapour density of aluminium chloride and of some organic derivatives of aluminium, and its specific heat indicate a value of approximately 27 for the atomic weight. The exact atomic weight

has been determined by measurement of the amount of hydrogen evolved by the action of acids or alkalis, and from the weight of silver chloride or bromide obtained from known weights of aluminium chloride or bromide. The value at present approved by the International Committee is 26.98, and is based on the determinations made by Krepelka by the silver method and on mass spectrograph measurements by Maltauch and Ewald.

### § 12 Aluminium Hydride, Nitride and Carbide

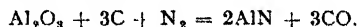
**Aluminium hydride**,  $(\text{AlH}_3)_n$ , results when lithium hydride (page 608) is treated with excess of aluminium chloride in ether. A more satisfactory preparation is to treat lithium aluminium hydride (*vide sub*) with aluminium chloride in ether:



Aluminium hydride is obtained from solution in ether as a white solid, a polymer of uncertain molecular weight; in solution it is probably the monomer  $\text{AlH}_3$ .

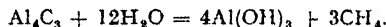
**Lithium aluminium hydride**,  $\text{LiAlH}_4$ , is obtained by the action of lithium hydride on aluminium chloride, the lithium hydride being in excess. It is a colourless solid which reacts violently with water and, like aluminium hydride, is a powerful reducing agent. It is now extensively employed in organic chemistry where it is a valuable reagent; care is necessary in its use, however, on account of the extreme violence of its action on water and similar substances.

**Aluminium nitride**,  $\text{AlN}$ , is formed when alumina is heated with carbon to  $1800^\circ$  in an atmosphere of nitrogen:



This reaction is the basis of the proposed *Serpek process* for the fixation of nitrogen since, with water, aluminium nitride yields ammonia and aluminium hydroxide and thus it was hoped to use it for the production of ammonia and, simultaneously, for the purification of bauxite. The method was not, however, a commercial success.

**Aluminium carbide**,  $\text{Al}_4\text{C}_3$ , is a yellowish powder, made by heating alumina and carbon to a very high temperature. It is decomposed by water, forming methane (page 370)

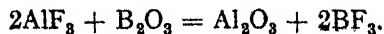


This reaction shows it to be a *methanide* whereas, in comparison, calcium carbide is evidently an *acetylide* (page 375).

### § 13 Aluminium Oxide and Hydroxide

#### Aluminium Oxide, $\text{Al}_2\text{O}_3$

Aluminium oxide, or alumina, occurs in nature as colourless crystalline corundum and, tinted with various metallic oxides, as ruby, sapphire, amethyst, emery, etc. Alumina is prepared as a white powder by the ignition of aluminium hydroxide, aluminium nitrate, or ammonia alum. Alumina fuses at  $2050^\circ$ , and it begins to volatilize appreciably at  $1750^\circ$ ; it boils at  $2250^\circ$ . Alumina is prepared in a crystalline condition by strongly heating a mixture of aluminium fluoride and boric oxide.



Artificial rubies have also been prepared: an ingenious method for doing this is due to Verneuil. In this a rod of alumina is heated by an inverted oxy-hydrogen flame, and a little finely powdered alumina and chromic oxide are sprinkled in the flame. These small particles melt and adhere to the rod, and thus build up a single crystal of alumina coloured by the chromic oxide—an artificial ruby. Artificial jewels made in this way are used for the bearings of watches.

Aluminium oxide is a stable and unreactive substance. It is only reduced with great difficulty.

When alumina is heated above about  $800^{\circ}$  an exothermal change takes place: the alumina changes in some way, for it then becomes almost insoluble in acids; its specific gravity rises rapidly from 2.8 to 4.0; and other physical properties change at the same time. The change is probably caused by the formation of a polymorphic modification of alumina.

Apart from its use in the manufacture of aluminium, bauxite is used in making the so-called bauxite bricks, and for lining the beds of basic open-hearth furnaces. Fused alumina is also used as a high-grade refractory for muffles, etc.

Alumina is now used in a process known as *chromatography* in which its property of selective adsorption is made use of, and by its use some remarkable separations have been effected.

Alumina is a constituent of aluminous cements which are coming into increasing use, being characterized by their quick-setting properties and resistance to sea-water.

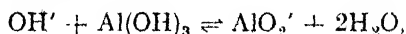
**Aluminium hydroxide**,  $\text{Al}(\text{OH})_3$ , is obtained as a colloidal precipitate when ammonia or an alkaline carbonate is added to a solution of an aluminium salt. It exists in at least two polymorphic crystalline forms, as well as colloidal and amorphous.

Freshly precipitated aluminium hydroxide dissolves easily in acids and in alkaline hydroxides. If the precipitate has stood a long time under water, or if the precipitate be dried, it dissolves very slowly in these reagents.

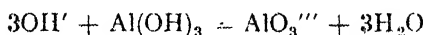
When aluminium hydroxide is precipitated in a solution containing a colouring matter, the latter is simultaneously precipitated, and the aluminium hydroxide with the adsorbed colouring matter is called a lake. Advantage is taken of this property in dyeing cloth. The aluminium hydroxide is first precipitated in the fibres of the cloth, and the fabric is then immersed in the dye, and some of the dye is fixed by the aluminium hydroxide in the fibres. An example of the use of aluminium hydroxide in this way is in the dyeing of cotton with alizarin, giving the well-known "turkey-red" colour. Hence, aluminium hydroxide is a dye-fixing agent or mordant. Dyes which stain the fibres directly need no mordant and are known as direct or substantive dyes.

Aluminium hydroxide is amphoteric for it will easily react with, and form salts with, both acids and alkalis. Both aluminium and the

oxide and the hydroxide will react with solutions of the caustic alkalis, forming solutions of sodium or potassium aluminates (e.g.,  $\text{NaAlO}_2$ ), and aluminates of the alkaline earths are also known. In solution the aluminates are believed to be *meta*-aluminates (e.g.,  $\text{NaAlO}_2$ ) and not ortho-aluminates (such as  $\text{Na}_3\text{AlO}_3$ ) because the freezing point of a solution of alkali is unaltered by dissolving alumina in it. If hydroxyl ions are replaced by  $\text{AlO}_2$  ions this would be accounted for:



whereas



would replace three hydroxyl ions by one  $\text{AlO}_3'''$ , thus altering the freezing point of the solution. The aluminates are not very stable; their aqueous solutions are strongly alkaline, on account of hydrolysis, and they are decomposed by carbon dioxide with the precipitation of aluminium hydroxide.

The minerals *spinel*— $\text{MgO} \cdot \text{Al}_2\text{O}_3$ , or  $\text{Mg}(\text{AlO}_2)_2$ , *chrysoberyl*— $\text{BeO} \cdot \text{Al}_2\text{O}_3$ , or  $\text{Be}(\text{AlO}_2)_2$ ; *gahnite*— $\text{ZnO} \cdot \text{Al}_2\text{O}_3$ , or  $\text{Zn}(\text{AlO}_2)_2$ , *hercynite*— $\text{FeO} \cdot \text{Al}_2\text{O}_3$ , or  $\text{Fe}(\text{AlO}_2)_2$ —are supposed to be *meta*-aluminates.

*Pleonaste* or *ceylonite*,  $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ ; *franklinite*, impure  $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ ; *magnesioferrite*,  $\text{MgO} \cdot \text{Fe}_2\text{O}_3$ , *magnetic oxide of iron*,  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ , and *chromite*,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$  are sometimes included in this group of minerals with the general name *spinel*s and general formula  $\text{R} \cdot \text{O} \cdot \text{R}'_2\text{O}_3$ , where  $\text{R}'$  represents the dyad elements Fe, Mn, Mg, Be, Zn, and  $\text{R}$  the triad elements Fe, Mn, Al, Cr.

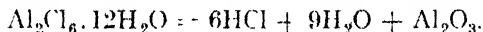
## § 14 Salts of Aluminium

Aluminium salts are usually colourless and are not poisonous. Since aluminium hydroxide is a very weak base, the salts with strong acids are very readily hydrolysed with water, and salts with weak acids can only be obtained, if at all, with great difficulty.

**Aluminium fluoride**,  $\text{AlF}_3$ , can be made by dissolving alumina in hydrofluoric acid; it is manufactured in quantity for the production of synthetic cryolite,  $\text{Na}_3\text{AlF}_6$ , for use in the extraction of the metal (page 744) by the interaction of aluminium fluoride, ammonium fluoride and sodium nitrate. Cryolite is also manufactured by heating a mixture of sodium aluminate and ammonium fluoride.

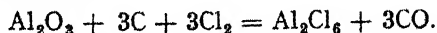
### Aluminium Chloride, $\text{Al}_2\text{Cl}_6$

Aluminium reacts with hydrochloric acid and the resulting aqueous solution, in presence of excess of acid, deposits crystals of  $\text{Al}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ . On heating, the hydrate decomposes, leaving alumina:



Anhydrous aluminium chloride is made on a large scale by passing chlorine over a mixture of carbon and alumina at a high temperature.

The chloride sublimes and is condensed in a receiver carefully protected against access of moisture:



Anhydrous aluminium chloride can also be made in the laboratory by passing chlorine or hydrogen chloride over heated aluminium turnings. (Fig. 32.2.)

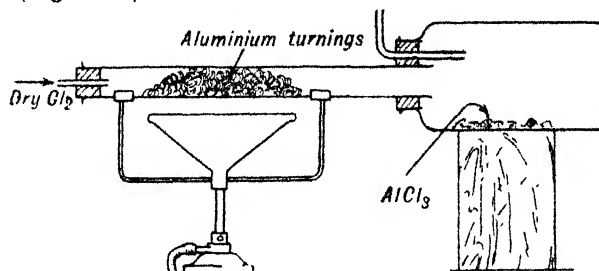
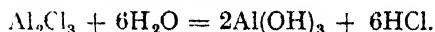
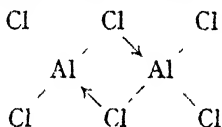


FIG. 32.2 — Preparation of Aluminium Chloride

Anhydrous aluminium chloride fumes strongly in moist air, owing to the formation of hydrogen chloride:

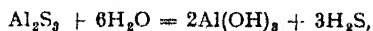


It sublimes at  $183^\circ$  and the vapour density, at about  $200^\circ$ , corresponds to the formula  $\text{Al}_2\text{Cl}_6$ . At temperatures above  $400^\circ$  dissociation begins and is complete at  $800^\circ$ . It seems almost certain that aluminium chloride, in the absence of water, has a covalent structure; this is supported by the facts that it is relatively volatile, it is soluble in many organic solvents and the pure liquid is a non-conductor. It is probably best represented by the formula



Aluminium chloride is an important catalyst in the Friedel-Crafts reaction in organic chemistry. A crude aluminium chloride, made from bauxite, is used in the petroleum industry in the manufacture of "synthetic" lubricating oils.

**Aluminium sulphide**,  $\text{Al}_2\text{S}_3$ , is a greyish-black powder which can be obtained by direct combination of the elements at a high temperature; by heating very strongly a mixture of alumina, carbon and sulphur; and by heating aluminium with iron pyrites. It is decomposed by water with evolution of hydrogen sulphide:



and hence, in qualitative analysis, the action of hydrogen sulphide, or ammonium sulphide, on an aluminium salt in solution precipitates the hydroxide.



### § 15 Aluminium Sulphate. The Alums

#### Aluminium Sulphate, $\text{Al}_2(\text{SO}_4)_3$

This salt is prepared by dissolving the hydrated oxide in sulphuric acid. Large quantities too are made by dissolving bauxite, and the purer varieties of clay, in the same acid. Clay roasted at a dull red heat is more readily attacked by the acid. The crude aluminium sulphate so obtained is called "alum-cake," and if much iron is present, "alum ferric cake," used in the purification of sewage on account of its power of precipitating colloids (cf., page 281).

A purer sulphate is made by heating bauxite with sodium carbonate, or by boiling cryolite with milk of lime. In each case a solution of sodium aluminate— $\text{Al}_2\text{O}_3 \cdot 3\text{Na}_2\text{O}$ —almost free from iron is obtained. The sodium aluminate is then decomposed by a current of carbon dioxide, and the precipitated aluminium hydroxide is dissolved in sulphuric acid. When the solution is concentrated, the mass solidifies to a white solid which does not crystallize very readily. The crystalline sulphate has the composition represented by:  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .

The salt is very soluble in water and has an acid reaction on account of hydrolysis. Basic sulphates are formed by boiling the normal sulphate with freshly precipitated aluminium hydroxide.

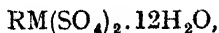
Aluminium sulphate is used in "foam" fire extinguishers, since when mixed with sodium bicarbonate carbon dioxide is formed along with aluminium hydroxide which renders the bubbles stable, and hence a stable foam results. This foam is particularly valuable for the extinction of oil fires.

It is also employed in sizing paper, tanning leather, waterproofing cloth and as a mordant in dyeing and in the purification of water supplies (page 307).

#### Alums

When hot solutions of equimolecular quantities of aluminium sulphate and potassium sulphate are mixed and the solution is cooled, octahedral crystals of a double sulphate of aluminium and potassium separate. The octahedral form is not always recognizable directly on account of the abnormal development of one or more faces. Thus, shapes like Fig. 32.3 may be obtained. The salt has the formula  $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

It is a typical member of a large number of isomorphous compounds which are called "alums." Their general formula is:



where R represents an atom of a univalent metal or a radicle—lithium,

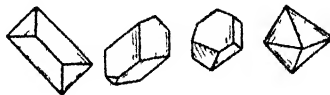


FIG. 32.3.—Abnormally developed Alum Crystals

potassium, sodium, ammonium, rubidium, caesium, and univalent thallium; and M represents an atom of a trivalent metal—aluminium, iron, chromium, manganese, cobalt, rhodium, indium, gallium, titanium, vanadium, and trivalent thallium. An iridium rubidium alum has also been reported. The report of a silver alum has not been confirmed.

Potash alum or *kalinite* occurs native as the result of the weathering of iron pyrites and alkali rocks. Mixed crystals of different alums are readily obtained by allowing mixed solutions of different alums to crystallize; and crystals of one alum, say chrome alum, grown on the surface of ordinary alum, or conversely, can be obtained. A series of **selenium alums** has also been made in which the sulphur atom is replaced by an atom of selenium. The selenium alums are isomorphous with the alums proper.

The stability of the alums generally decreases with increasing atomic weight of the trivalent metal, and increases in stability with increasing atomic weight of the univalent metal. For example, sodium forms alums only with the lightest trivalent metals - aluminium, vanadium, and chromium; potassium forms stable alums only with aluminium and chromium. The ferric and gallic alums readily form basic salts; and indium does not form a potash alum, but gives instead the double sulphate  $K_2SO_4 \cdot In_2(SO_4)_3 \cdot 6(\text{and } 8)H_2O$ ; titanium forms an alum only with caesium and rubidium. Lithium alum has been made only recently, and soda alum is not easy to make. The alums are usually much more soluble in hot water than in cold; and they are deposited from cooling concentrated solutions of the two salts in the form of octahedral or cubical crystals.

When heated, the alums give up their water of crystallization. Potash-alum liquefies at  $92^\circ$ , and slowly loses all its water of crystallization at  $100^\circ$ ; at higher temperatures, the water is driven off more rapidly, and leaves behind a white porous mass called "burnt alum." Ammonia alum when calcined gives a residue of alumina— $Al_2O_3$ —which may contain traces of sulphates. The soluble sulphates can be removed by washing.

**Alum-stone** or *alunite* is a kind of basic alum— $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$ —found near Rome, and in Hungary, etc. It is supposed to have been formed by the action of volcanic sulphur dioxide on the felspathic rocks. It is insoluble in water, but, on calcination, it gives a residue of alumina (mixed with ferric oxide as impurity) and potash-alum passes into solution when the mass is digested with water. Alum prepared in this way is called "Roman alum," and that which occurs in commerce is crystallized in cubes.

Alum is extensively used as a mordant in dyeing and in the leather industry. On account of its power of precipitating colloids, it is used in styptic pencils, etc., for stopping bleeding from small cuts since it causes coagulation of the blood.

### Pseudo-alums

A series of double sulphates, sometimes called pseudo-alums, can be made by introducing a bivalent element—manganese, ferrous iron, copper, zinc, magnesium—in place of the univalent element of ordinary alums. Thus,



The latter is related to the mineral *halotrichite*. These alums are not isomorphous with ordinary alums.

**Aluminium silicates** are important constituents of various minerals, e.g., the feldspars, micas, garnets and zeolites. The feldspars, such as *orthoclase* or potash feldspar ( $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ), form part of most igneous rocks; the micas are double silicates of aluminium and another metal such as magnesium; and the garnets are double silicates of aluminium (or another trivalent metal) and a divalent metal (e.g., Ca, Mg, or Fe). The zeolites are hydrated double silicates of a metal and aluminium. The sodium compound ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 6\text{H}_2\text{O}$ ), known as sodium *permutit*, is used for water-softening (page 311). Alumino-silicates are also important constituents of clays, which are discussed on page 776.

Aluminium silicates have now come into use as fillers in artificial rubbers, particularly those used for shoe soles and flooring.

## § 16 Detection and Determination of Aluminium

Aluminium salts are usually recognized in qualitative analysis by the formation of a white, gelatinous precipitate of the hydroxide on addition of ammonia and ammonium chloride. In presence of litmus solution, a "lake" is formed. Alumina, when moistened with cobalt nitrate solution and heated on charcoal, gives a bright blue infusible mass.

Aluminium has usually been determined by precipitation as the hydroxide with ammonia and ammonium chloride, followed by ignition to the oxide. Recently precipitation by "oxine" (8-hydroxy quinoline) has been advocated.

## § 17 Gallium, Indium and Thallium

The rare metal **gallium**, Ga, was discovered by Lecoq de Boisbaudran in 1875 while studying a zinc blende from the Pyrenees. It occurs widely in minute quantities. Thus it has been found in the mineral germanite (page 782) to the extent of 0.5 per cent and also (up to 0.03 per cent) in the ash of certain coals. Bauxite usually contains small amounts and it occurs in traces in zinc blende. The zinc resulting, if distilled, leaves a residue of lead which contains up to 0.1 per cent of gallium and this, along with the ash of Northumbrian coals, is the principal source of gallium. The ash also contains germanium (page 782); after this has been removed gallium chloride is extracted from the residue with isopropyl ether. The metal can be obtained by electrolysis of an alkaline solution of the salt. It is a

soft metal and is notable for its very low melting point,  $29.8^{\circ}$ ; it boils at  $2100^{\circ}$ .

There are but few commercial uses for gallium partly because the liquid metal attacks most metals and reacts with most refractory materials at high temperatures unless completely protected from oxidation. Its property of not "wetting" quartz has enabled a thermometer, using gallium, alloyed with a small quantity of indium and tin, in quartz, to be used for temperatures up to  $1000^{\circ}$ .

**Indium**, In, is another rare metal discovered in 1863 by T. Reich and F. Richter in a zinc ore from Freiberg. All commercial tin contains indium, and the mineral *cythndrite* from Bolivia contains up to 1 per cent of it.

The principal "source" of indium is the lead obtained during the purification of zinc (cf. gallium, *supra*). This is cupelled and almost all the indium is found in the litharge formed. The indium present is then converted into the sulphate and the metal is obtained by electrolysis. Like gallium it is a soft metal with a relatively low melting point,  $156.4^{\circ}$ ; it boils at  $2100^{\circ}$ . The spectrum of indium contains a prominent indigo blue line which is the origin of its name.

Very few uses of indium have been found. A very thin layer (0.0001 in. thick) is used as a plating on the surface of some lead containing bearing metals for aircraft since lead is attacked by lubricating oils.

Gallium and indium metals are not attacked by water, although thallium slowly decomposes water at ordinary room temperatures. Gallium and indium are attacked by nitric acid, whereas aluminium under the same conditions appears to be passive. Gallium and indium are related to aluminium much as zinc is related to magnesium. Aluminium, gallium, and thallium form oxides  $R_2O_3$ . The hydroxides  $R(OH)_3$  have weak acidic and basic properties. All three elements form well-defined isomorphous ammonia alums. Unlike gallium chloride  $GaCl_3$ , and aluminium chloride,  $AlCl_3$ , indium chloride,  $InCl_3$ , can be obtained by the evaporation of the aqueous solution at  $100^{\circ}$  with relatively little hydrolysis. All three elements are trivalent, but indium also forms three chlorides:  $InCl$ ,  $InCl_2$ , and  $InCl_3$ ; and gallium forms  $GaCl$  and  $GaCl_2$ .

**Thallium**, Tl, was discovered by W. Crookes in 1861 while studying the flue dust from a sulphuric acid chamber at Tilvertope (Hartz mountains). Thallium occurs associated with pyrites in zinc ores, and in the mineral *crookesite*, a copper selenide containing 16 to 18 per cent of thallium, and 3 to 5 per cent of silver. Thallium was discovered by the spectroscope. Its spectrum has a characteristic green line—hence its name is derived from the Greek *θαλλός* (*thallos*), a green twig.

Thallium is extracted from the flue dust by leaching with dilute sulphuric acid; hydrogen sulphide is passed in to precipitate such metals as lead and tin. The filtrate is concentrated and the thallium precipitated as its chloride, which is insoluble. This is converted to the sulphate which is purified by recrystallization and the metal recovered by electrolysis or by precipitation by zinc. Thallium is a soft, white metal which marks paper like lead. It melts at  $304^{\circ}$  and boils at  $1457^{\circ}$ .

Thallium shows resemblances to a number of metals outside its own "family". The free metal closely resembles lead; in its univalent condition, it displays analogies with the alkali metals and with silver and mercurous mercury.

The thallous halides, for instance, like those of silver, are but slightly soluble in water. Mercurous, thallous and silver chlorides are soluble in a solution of sodium thiosulphate. Thallous sulphide, like the silver and lead sulphide, is but sparingly soluble in water; and thallous hydroxide and carbonate are fairly soluble in water. The thallic salts are not very stable, and they behave somewhat like the auric salts, so that while thallous oxide,  $Tl_2O$ , is a strong base, the trioxide,  $Tl_2O_3$ , is a feeble base.

The tervalent salts also show resemblances to lead, as well as to aluminium, gallium and indium.

Recently thallium and its compounds have found uses technically. Thus thallous carbonate prevents the growth of mildew in textiles. Some thallium compounds have antiknock properties and an alloy of thallium, aluminium and silver in the proportions of 1:1.8 has remarkable resistance to tarnishing.

Addition of thalious iodide causes a marked increase in the sensitivity of silver iodide emulsions to light. Certain thallium salts have been used as depilatories and their administration to sheep in order to induce an artificial moult has been proposed in order to avoid the necessity for shearing. The poisonous nature of thallium compounds renders these uses unprofitable. Thallium itself is used to a limited extent in the production of a very refractive optical glass, and as the oxysulphide in the "thalofide" photo-electric cell.

## CHAPTER 33

# SCANDIUM, YTTRIUM, LANTHANUM, THE RARE EARTHS (LANTHANONS) AND THE TRANS-URANIUM ELEMENTS

### § 1 Group IIIA of the Periodic Table

THE elements scandium, yttrium, lanthanum and the rare earths (now, following a suggestion by J. K. Marsh in 1948, usually known as the *lanthanons*) comprise Group IIIA of Mendeléeff's classification although strictly speaking Mendeléeff's table made no provision for the rare earths nor, for obvious reasons, for the trans-uranium elements.

The three elements scandium, yttrium and lanthanum are related to the aluminium family, but they occur in association with the lanthanons and their properties closely resemble those of the lanthanons. Hence, at one time they were classified along with the rare earths (in particular yttrium), but now that more is known about the structure of the atoms of these elements (*cf.* page 150 and § 5 below) they are known to be correctly considered separately.

Scandium and yttrium are, strictly, transition elements, that is elements in which the penultimate quantum group of electrons is being enlarged in passing from one element to the next in order of atomic number. In the lanthanons it is the antepenultimate group which is undergoing this expansion (page 153). Although it can thus be seen why scandium and yttrium are classified apart from the lanthanons it can also be understood why there are marked resemblances in properties among them all.

### § 2 Scandium, Yttrium and Lanthanum

All three of these elements occur, along with the lanthanons and with titanium, zirconium, hafnium and thorium, which are elements of Group IV of the Periodic Table and which are discussed in the next chapter. Scandium also occurs, along with tungsten, in wolframite, and this is the most accessible source.

Scandium, yttrium and lanthanum are all trivalent elements; they thus form oxides of the general type  $M_2O_3$  and chlorides  $MCl_3$ . Their hydroxides are all basic and are insoluble in a solution of sodium hydroxide. The basic character of these oxides increases from scandium to lanthanum. Thus scandium oxide is a very weak base whereas lanthanum oxide reacts directly with water, with evolution of heat, to form the hydroxide. All three elements form stable carbonates; their halides are non-volatile and are not hydrolysed by water. They form double sulphates, such as  $La_2(SO_4)_3 \cdot 3K_2SO_4$ , but these are not alums.

### § 3 Actinium

Actinium, like radium, its analogue in Group II, is radioactive. It is doubtful if it has been obtained in a state of purity and its interest is in its radioactive properties.

It was discovered in 1899 by Debierne (a collaborator of Madame Curie). It is found in the filtrate from the precipitation of polonium in the extraction of that element from pitchblende (page 881). Actinium is exclusively trivalent and in

chemical properties closely resemble lanthanum and the rare-earths. It stands in the same relation to the trans-uranium elements (or actinons, *sub* § 7) as lanthanum does to the lanthanons (§ 4).

## § 4 The Lanthanons or Rare-earth Elements

The group of elements known as the rare-earths comprises a series of elements so closely similar in properties that their separation is extremely difficult and, until the work of Mosley (page 136), it was uncertain how many definite and distinct elements exist.

The lanthanons occur in a number of minerals, some of which are uncommon. The most important source of these elements is *monazite*, a complex phosphate containing yttrium, thorium, zirconium, and titanium along with the lanthanons, *cerite*, cerium silicate mixed with silicates of other lanthanons, *gadolinite*, a basic silicate containing also beryllium and iron, and *fergusonite*, a tantalum-niobate containing up to 40 per cent of the lanthanons. Monazite sand is found in considerable quantities in India and Brazil and the U.S.A. and is worked principally for thorium. The former term "rare-earths" is now seen to be a misnomer for many of these elements are more plentiful than some others which, owing to their being familiar, are not thought of as being scarce. Thus cerium is believed to occur in the earth's crust to a greater extent than tin or lead and even thulium, one of the scarcest of the lanthanons, is as abundant as iodine.

### History

In 1794 J. Gadolin discovered a new earth in the mineral, gadolinite, which had been named in honour of himself; and in 1797 A. G. Ekeberg named the new earth *yttria*, after Ytterby, the place in Sweden where the mineral was found. C. G. Mosander (1843) noticed that what was then called *yttria* is really a complex earth containing *yttria* proper, and two other earths, which were oxides of two new elements, **erbium** and **terbium**. In 1880 P. T. Cleve found that **erbium** earth not only contained erbium, but also a new element **thulium**—a name derived from the old Latin *Thule* for the uttermost north—and **holmium**. In 1905 G. Urbain also discovered lutecium in the *yttria* earths. In 1886 Lecoq de Boisbaudran separated **dysprosium**—from the Greek *δύσπρος* (*dyspros*), difficult, in allusion to the trouble involved in its isolation—from the same earth. In the same year, C. Marignac and Lecoq de Boisbaudran showed that **terbium** earth contained a new element **gadolinium** as well as terbium. In 1878 C. Marignac found the oxide of a new element in gadolinite. Thus he named **ytterbium**, after Ytterby (Sweden). In 1879 L. F. Nilson, while extracting *ytterbia* from the mineral *euxenite*, also separated an unknown earth which he called **scandium**, in honour of his country—Scandinavia—where the mineral was found. In 1839 C. G. Mosander separated the oxide of a new element from an earth which had hitherto been thought to be *ceria*. This earth he named **lanthanum**, *λανθάνειν* (*lanthanein*), to hide. In 1841 C. G. Mosander separated another earth—*didymia*—from lanthanum. The corresponding element was called **didymium**—from the Greek *διδυμος* (*didymos*), a twin, a name suggested by its close relationship and almost invariable occurrence with lanthanum.

By fractional precipitation, Lecoq de Boisbaudran, in 1879, separated **samarium** from **didymium** (discovered by C. G. Mosander in 1841). Samarium was named after the mineral *samaraskite* which, in turn, was named after a Russian, M. Samarsky. E. Demarçay, in 1901, separated **europium** from samarium; the residual *didymia* was supposed to be the oxide of a distinct metal, **didymium**, with a definite atomic weight and which furnished salts whose aqueous solutions gave a characteristic absorption spectrum. In 1885, by the fractional crystallization of a nitric acid solution of **didymium ammonium tartrate**, A. von Welsbach separated this salt into two other salts, one bright green and the other amethyst blue. The corresponding oxides were respectively pale green and pale blue. The metal derived from the pale green oxide was called **praseodymium**—from the





These facts can be seen clearly in Table XLVII which shows the electronic structure of the atoms of the elements scandium, yttrium and the lanthanons.

TABLE XLVII

Element	Number of electrons in shell													
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s
Scandium . . . . .	2	2	6	2	6	1	2							
Yttrium . . . . .	2	2	6	2	6	10	2	6	1		2			
Lanthanum . . . . .	2	2	6	2	6	10	2	6	10		2	6	1	2
Cerium . . . . .	2	2	6	2	6	10	2	6	10	1	2	6	1	2
Praseodymium . . . . .	2	2	6	2	6	10	2	6	10	2	2	6	1	2
Neodymium . . . . .	2	2	6	2	6	10	2	6	10	3	2	6	1	2
Promethium . . . . .	2	2	6	2	6	10	2	6	10	4	2	6	1	2
Samarium . . . . .	2	2	6	2	6	10	2	6	10	5	2	6	1	2
Europium . . . . .	2	2	6	2	6	10	2	6	10	6	2	6	1	2
Gadolinium . . . . .	2	2	6	2	6	10	2	6	10	7	2	6	1	2
Terbium . . . . .	2	2	6	2	6	10	2	6	10	8	2	6	1	2
Dysprosium . . . . .	2	2	6	2	6	10	2	6	10	9	2	6	1	2
Holmium . . . . .	2	2	6	2	6	10	2	6	10	10	2	6	1	2
Erbium . . . . .	2	2	6	2	6	10	2	6	10	11	2	6	1	2
Thulium . . . . .	2	2	6	2	6	10	2	6	10	12	2	6	1	2
Ytterbium . . . . .	2	2	6	2	6	10	2	6	10	13	2	6	1	2
Lutecium . . . . .	2	2	6	2	6	10	2	6	10	14	2	6	1	2

In one or two instances, namely, neodymium, samarium, europium, thulium and ytterbium, the experimental evidence is not sufficient at present to confirm every detail of these structures but those given above are believed to be the most probable.

The lanthanon group of elements is thus defined and is seen to consist of the elements from lanthanum to lutecium inclusive, in all of which the electronic arrangement of the outermost (6th quantum) and next to the outermost (5th quantum) shells are identical. It is foreshadowed by scandium and yttrium which precede lanthanum, vertically, in the Periodic Table as starting points of the first and second transition series respectively. The remarkable similarity in properties of the lanthanons is thus a consequence of the identity of the ultimate and penultimate electron shells of these elements.

The next element after lutecium is hafnium (atomic number 72) in which the fifth quantum group has begun to expand, making the structure (2.8.18.18.32.10.2), so that hafnium is not a lanthanon and differs from the lanthanons in chemical properties; it is, in fact, a transition element.

## § 6 The Isolation of the Lanthanide Elements

The isolation of the individual elements of this group has been the subject of extensive investigation and, until recently, it has been a most laborious and difficult operation on account of the extremely close chemical resemblance between them.

The principal methods employed have been based on differences in the solubility of suitable salts, variation in basic character, valency differences and variable ease of amalgam formation. Of these, fractional crystallization of salts, including some double salts such as double sulphates with the alkali metals, salts of dimethyl phosphoric acid  $(\text{CH}_3\text{O})_2\text{PO.OH}$ , which show a regular diminution of solubility from lanthanum to lutecium and complex salts of ethylene diamine tetracetic acid have yielded promising results. But in the end, the process is inevitably tedious and lengthy.

For the production of small quantities of very pure salts of the lanthanons the use of ion-exchange methods has become important. The mixture of lanthanons in the form of a neutral solution of their nitrates is introduced into the top of a column of a suitable cation-exchange resin in its hydrogen form. The lanthanons are adsorbed on the column and are selectively eluted from the column by means of citric acid solutions of 5 per cent concentration, adjusted to be only slightly acid, by means of ammonia. By suitable adjustment of the *pH* of the citric acid solution the lanthanons can be selectively removed from the column beginning with the element of largest atomic number. The first successful separation of promethium (*vide supra*) was effected in this way.

A further method which is being investigated is the extraction, on the counter-current principle, of aqueous solutions of lanthanon nitrates by means of *n*-butyl triphosphate, and this seems to be a promising method also.

The rare-earth metals can be extracted from their oxides by the aluminothermic method or by reduction with sodium. An alloy of cerium, lanthanum, praseodymium, neodymium, etc., is made in this way from the residues left after the extraction of the thorium from monazite and is known as *mischmetall*. It is used as a reducing agent for the reduction of refractory oxides such as magnesia. Mischmetall, and cerium-iron alloys, are also used for the so-called "flints" of petrol-lighters, etc. Ceria, mixed with 99 per cent of thoria, is used in incandescent gas mantles (page 806). Some of the rare-earth compounds have been used for colouring porcelain, and solutions of ceric compounds (e.g., ceric sulphate) are used as oxidizing agents in volumetric analysis. Lanthanum tungstate is used in the production of Crookes glass upon which it confers the property of absorbing ultra-violet light.

## § 7 The Trans-Uranium Elements

Before 1940 no element was known with an atomic number greater than 92 or an isotope of mass number more than 238. Since that time ten more elements, with atomic numbers up to 102 and mass numbers to 255, have been made artificially as described in Chapter 12. These elements form part of an inner-transition group, analogous to the lanthanons, but there is still controversy as to where the inner-transition begins.

There is general agreement about the structure of radium (whose atomic number is 88). In this element the first four quantum groups have been filled and the fifth, sixth and seventh have the arrangement (2.6.10).(2.6)(2). With the next element, actinium, transition elements begin and the structure (2.6.10).(2.6.1)(2). for the arrangement in the last three quantum groups is accepted. The next element is thorium and, according to one view, the inner-transition begins with this element, alternatively, the view is held in some quarters that the ordinary transition continues until proactinium, making uranium the first element in which the fifth quantum group begins to expand. So far, the experimental data are insufficient to decide decisively between these views (the comparison of which can be understood from Table XLVIII, which sets out the electronic structures of the relevant elements according to the two theories). At present, it seems that the former scheme in which the inner-transition begins with thorium, is the more favoured; hence the name *actinons* which (by analogy with the lanthanons) has been applied to these elements. These structures have, for the same reason, been incorporated into Table XII on pages 150-1.

It seems likely that the element with atomic number 103 will have sixth quantum group completely filled (i.e. with 14 *5f* electrons); it will therefore be of great interest to discover the nature of the next element after that to see whether it is an ordinary transition element like hafnium or whether in this period more than 32 electrons can be incorporated into the fifth quantum shell.

All the trans-uranium elements are radioactive with comparatively short half-lives. They are thus unlikely to occur naturally to any extent. Nevertheless,

TABLE XLVIII

INNER-TRANSITION BEGINNING AT THORIUM		INNER-TRANSITION BEGINNING AT URANIUM													
Element	Atomic Number	Number of electrons in shell													
		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f
Radium . . .	88	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Actinium . . .	89	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Thorium . . .	90	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Protoactinium . . .	91	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Uranium . . .	92	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Neptunium . . .	93	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Plutonium . . .	94	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Americium . . .	95	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Curium . . .	96	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Berkelium . . .	97	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Californium . . .	98	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Einsteinium . . .	99	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Fermium . . .	100	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Mendelevium . . .	101	2	2	6	2	6	10	2	6	10	14	2	6	10	2
Nobelium . . .	102	2	2	6	2	6	10	2	6	10	14	2	6	10	2

as in the left-hand portion of the Table

plutonium occurs in minute quantities in pitchblende and carnotite; very small amounts have been recovered from pitchblende residues left from the extraction of radium.

Of the elements mentioned in this section only the trans-uranium elements proper are further considered here; radium has been dealt with in Chapter 30, thorium is covered in Chapter 34 and uranium in Chapter 37.

These elements exhibit variable valency, so far as their properties have been examined; neptunium, plutonium, americium and curium are all trivalent; in addition the first three exhibit tetra-, penta- and hexavalency. The elements themselves have been obtained by reduction of the hexafluorides with barium; they are white and relatively low melting. Neptunium and plutonium, like uranium, form the ions  $\text{NpO}_2^{++}$  and  $\text{PuO}_2^{++}$  but their stability decreases with increasing atomic number. A considerable number of compounds has been investigated (a surprisingly large number when the minute quantities of the elements which are available are considered) and, as might be expected, their chemistry is very similar to that of uranium. It is quite clear from these investigations that the trans-uranium elements are not the analogues of rhodium and the platinum metals; thus, the view, based on such experimental evidence of a physical kind as is available concerning the electronic structure of these elements, that they are part of an inner-transition series like the lanthanides, is confirmed by the chemical evidence.

### § 8 Relationships of the Elements of Group III

The exact sub-classification to be adopted in this group has in the past occasioned some difficulty, but it is now generally agreed that boron and aluminium are best associated with gallium, indium and thallium. This is supported by the conclusions at present accepted for the electronic configurations of these elements which are given in Table XLIX.

TABLE XLIX

Element	Number of electrons in orbit														
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p
Boron . . . .	2	2	1												
Aluminium . .	2	2	6	2	1										
Gallium . . .	2	2	6	2	6	10	2	1							
Indium . . . .	2	2	6	2	6	10	2	6	10		2	1			
Thallium . . .	2	2	6	2	6	10	2	6	10	14	2	6	10	2	1

The variation in the physical properties of the five elements boron, aluminium, gallium, indium and thallium with increasing atomic weight is indicated in Table L.

TABLE L.—PROPERTIES OF THE BORON-ALUMINIUM FAMILY

	Boron	Aluminium	Gallium	Indium	Thallium
Atomic weight .	10.82	26.98	69.72	114.82	204.39
Specific gravity .	2.33	2.7	5.9	7.3	11.85
Atomic volume .	4.6	10.0	11.8	15.6	17.3
Melting point .	2100°	660°	29.8°	156.4°	304°

With the exception of boron and aluminium, the elements of this series are scarce and rare. The oxides of the metals from aluminium to thallium are obtained by adding ammonia to solutions of salts of the metals. The oxides dissolve in acids, forming salts. The haloid salts are volatile. At about  $100^{\circ}$  thallic chloride breaks down into thalious chloride and chlorine. The chlorides readily form complex salts with other chlorides. The non-metallic characters predominate in boron, and it can almost be said that the properties of boron summarize those of the group, although any particularly striking family trait is wanting. Boric oxide exhibits definitely acidic and very feeble basic properties, for it combines with a few anhydrides—e.g.,  $P_2O_5$  and  $SO_3$ —of the strong acids to form compounds in which boron acts as a base. Thus *boron phosphate*,  $BPO_4$ , is a stable compound, so also is *boron sulphate*,  $B(HSO_4)_3$ , but is decomposed by heat or water. The other oxides are basic towards most acids, and the basic properties of the elements increase and the acidic properties decrease with increasing atomic weights in passing from aluminium to thallium. Thus, aluminium is acidic towards strong alkalis, gallium and indium hydroxides are soluble in concentrated potash solutions, and there is evidence of the formation of an unstable potassium thallate in the violet liquid which is produced when thallic hydroxide is suspended in a concentrated solution of potassium hydroxide, and treated with chlorine. The potassium hydroxide solution of indium oxide gives a precipitate of the oxide when boiled and the solution is decomposed by carbon dioxide. The trichloride,  $TlCl_3$ , for instance, is partially hydrolysed by water. When thallium is trivalent, its compounds resemble the other members of the group; the thallic salts are readily reduced to thalious salts. The . . . ic salts are usually soluble in water and, excepting boron, the elements can replace aluminium to form alums—e.g., *gallium alums*,  $MGa(SO_4)_2 \cdot 12H_2O$ ; *indium alums*,  $MIn(SO_4)_2 \cdot 12H_2O$ . The grouping of thallium with aluminium is justified by the fact that thallium sesquioxide can replace alumina in the alums. Aluminium, indium, and thallium form complex sulphates with the alkali sulphates crystallizing with eight molecules of water; but when univalent, thallium behaves like silver and the alkali metals. The kinship of the thalious and alkali salts is illustrated by the fact that (i) thalious salts are stable bodies and usually isomorphous with the corresponding potassium salts; (ii) thalious sulphate can take the place of the alkali metal to form alums—e.g.,  $Tl_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ ; (iii) thalious monoxide,  $Tl_2O$ , dissolves in water, forming a corrosive solution which resembles that obtained with caustic alkali—it forms salts when treated with acids; absorbs carbon dioxide, forming thalious carbonate; colours red litmus blue; the carbonate and phosphate are soluble; the chloroplatinate, like that of potassium, is sparingly soluble, etc.; (iv) it forms a tri-iodide, isomorphous with potassium tri-iodide; and (v) it can replace potassium in potassium chromate, forming  $TlKCrO_4$ . Thallium itself resembles lead.

The close relationship between scandium, yttrium and lanthanum and the metals of the rare-earths, and likewise between radium, actinium, thorium and the trans-uranium elements, has been discussed above, and seen to lie in the very similar structures of the atoms of these elements. They also resemble the other sub-group in being trivalent, and in other ways.

## CHAPTER 34

# SILICON, TIN AND LEAD, AND OTHER ELEMENTS OF GROUP IV

### § 1 Group IV of the Periodic Table

GROUP IV comprises the following elements, viz., carbon and silicon, with titanium, zirconium, hafnium, and thorium in the A sub-group; and germanium, tin and lead in the B sub-group.

The two short-period elements are more closely related to the B sub-group, and there is a marked gradation of properties in passing from carbon to lead. This gradation is of such a nature, however, that there are few, if any, obvious resemblances between the extreme members. Thus carbon and lead differ very considerably; far more, for example, than do lithium and caesium, or even beryllium and barium.

### § 2 Silicon, Si

#### History

Silicon does not occur free in nature, but numerous oxygen compounds are known. The process of manufacturing glass from silicates has been known from ancient times, and J. J. Becher (1669) believed that these silicates contained a peculiar earth which he called *terra vitrescibilis* (vitrifiable earth); this is now called "silica." It was known in the seventeenth century that Becher's vitrifiable earth does not fuse when heated alone, and that a fusible glass is formed when it is heated with other earths. O. Tachenius (1660) noticed that the vitrifiable earth had acid rather than alkaline properties; C. W. Scheele (1773) showed it to have the characteristics of a refractory acid; and J. L. M. Smithson (1811) considered it to be an acid rather than an alkaline earth. J. J. Berzelius prepared amorphous silicon in 1823; and H. St. C. Deville prepared crystalline silicon in 1854.

#### Occurrence

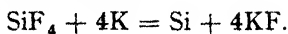
After oxygen, silicon is the most abundant element in the earth's crust, and silica is one of the most important compounds found in that crust. Silica occurs both free and combined with various bases. Silica occurs free as quartz, flint, sand; examples of natural silicates are *felspar* or *orthoclase*,  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ; *kaolinite*,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , and *anorthite*,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ .

### Preparation of Silicon

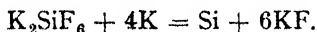
Two forms of silicon have been described, known as amorphous and crystalline silicon. It is doubtful, however, if these are true allotropic forms since X-ray examination has shown that both have the same structure (resembling that of the diamond) and the form which appears to be amorphous is, in fact, crystalline although finely divided.

### Amorphous Silicon

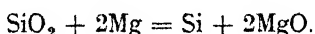
This can be made by heating potassium or sodium in an atmosphere of silicon chloride or silicon fluoride:



The brown mass so formed is washed with water and hydrofluoric acid, heated at a dull red heat, and finally washed and dried. It is also formed by heating a mixture of sodium or potassium fluosilicate with metallic potassium:

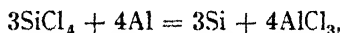


The brown mass is cleaned as before. Quartz is reduced to silicon when it is intimately mixed with magnesium powder and heated:

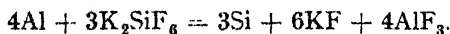


### Crystalline Silicon

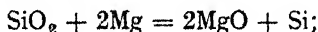
Crystalline silicon is made by dissolving silicon in molten metals, and on cooling, part of the silicon separates from the solution in a crystalline condition. By passing a stream of silicon tetrachloride vapour over aluminium previously melted in an atmosphere of hydrogen, the volatile aluminium chloride passes on, and the silicon liberated by the reaction



dissolves in the molten aluminium. As the molten aluminium cools, silicon separates in long lustrous crystals. The aluminium can be separated by treatment with hydrochloric acid. Crystalline silicon is also made by heating a mixture of potassium or sodium silicofluoride, or powdered silica, with an excess of aluminium:



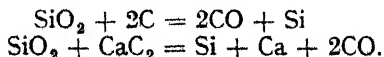
The silicon dissolves in the excess of molten aluminium. The cold solution is treated with hydrochloric acid to remove aluminium, and with hydrofluoric acid to remove silica. Silica is reduced when heated with metallic magnesium:



if an excess of magnesium be employed, magnesium silicide,  $\text{Mg}_2\text{Si}$ , is formed. Both it and magnesium oxide can be removed by treatment



with hydrochloric acid. Crystalline silicon is made commercially by heating silica with coke or calcium carbide in the electric furnace:



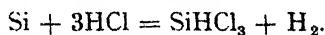
Excess of silica must be used or else silicon carbide (carborundum) is formed (page 769).

Silica is also reduced in the blast furnace (page 901), so that cast iron always contains silicon. Ferro-silicon alloys containing not more than 17 per cent of silicon can be made in a blast furnace; commercial alloys are available, containing up to 90 per cent of silicon, and are made by reduction of a suitable mixture of silica and iron oxide by means of carbon in an electric furnace.

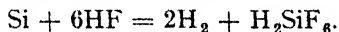
### Properties

As with carbon, the different forms of silicon differ in chemical as well as in physical properties.

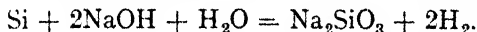
Amorphous silicon is a dark-brown amorphous powder with a specific gravity 2.4. It melts at  $1440^\circ$ , and volatilizes in the electric arc. When calcined in air, a surface skin of silica is formed which protects the element from complete oxidation. Silicon ignites in chlorine at about  $450^\circ$ , and burns to silicon tetrachloride. If silicon be heated with hydrogen chloride, free hydrogen and silicon chloroform are formed:



Silicon is insoluble in water and most acids; but it dissolves in hydrofluoric acid, forming hydrofluosilicic acid:



When boiled with alkaline hydroxides it forms hydrogen and alkaline silicate:



Crystalline silicon forms dark-grey opaque needle-like crystals or octahedral plates (cubic system). It is hard enough to scratch glass. Its specific gravity varies between 2.34 and 3, according to the temperature to which it has been heated. It burns when heated in chlorine and takes fire spontaneously in fluorine. Silicon is insoluble in most acids, but dissolves in a mixture of nitric and hydrofluoric acids. It melts at  $1440^\circ$ , and distils in the electric furnace (b.p.  $2600^\circ$ ). Crystalline silicon slightly conducts electricity, amorphous silicon does not. Chemically, crystalline silicon resembles amorphous silicon, but it is not so active. Silicon combines with nitrogen, forming **silicon nitride**, and also with the metals, forming **silicides**.

### Uses

Silicon prepared from quartz and coke in an electric furnace is used for making alloys: in particular, a silicon iron which is very resistant

to acids and is used, for example, in the distillation of nitric acid; and silicon bronze (a copper-tin alloy containing a trace of silicon, is used for telegraph and telephone wires). A silicon-iron alloy, containing 3-4 per cent of silicon, known as *stalloy*, has wide applications in the electrical industry on account of its very low hysteresis loss. Certain of the compounds of silicon, notably silica and carborundum, have many applications.

The use of silicon as a rectifier for the conversion of alternating to direct current for traction purposes is being actively investigated and an experimental train, using silicon for this purpose, is in service (1958). (Cf. page 782.)

In the last few years the *silicones* have become very important industrial products; they are, however, organic compounds of silicon and so do not fall within the scope of the present book.

### Atomic Weight

The vapour densities of volatile silicon compounds, and the position of silicon in the Periodic Table indicate a value of approximately 28 for the atomic weight of silicon. The best determinations of the combining weight have been made by determining the amount of silver halide produced by dissolving silicon chloride or bromide in water, followed by addition of silver nitrate. In conjunction with the value obtained by Whytlaw-Gray from the limiting density of silicane and from determinations of the abundance ratios of the isotopes by Bainbridge *et al.*, the value 28.09 has been recommended by the International Committee (1957).

## § 3 Hydrides and Carbides of Silicon

### Hydrides

Silicon forms a number of hydrides, similar in composition to the simpler hydrocarbons. It is evident, however, that the power possessed by carbon, of forming long chains of atoms, is exhibited by silicon only to a slight extent. Examples of silicon hydrides are:

Silico-methane, silicane or silane,  $\text{SiH}_4$ .

Silico-ethane,  $\text{Si}_2\text{H}_6$ .

Silico-propane,  $\text{Si}_3\text{H}_8$ .

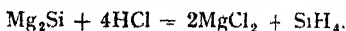
Silico-butane,  $\text{Si}_4\text{H}_{10}$ .

Silico-ethylene ( $\text{Si}_2\text{H}_4$ ) and silico-acetylene ( $\text{Si}_2\text{H}_2$ )<sub>n</sub> have been reported, but their existence is doubtful.

The hydrides of silicon are not very stable and, like many other hydrides, act as reducing agents.

#### Silico-methane, Silicane, $\text{SiH}_4$

This gas can be made mixed with hydrogen and other hydrides of silicon by the action of concentrated hydrochloric acid on magnesium silicide:

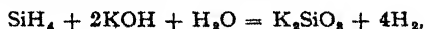


Magnesium silicide is obtained by heating sand with excess of magnesium powder. It is best made by reducing silicon tetrachloride with lithium aluminium hydride.

Silico-methane is a colourless gas, not spontaneously inflammable at ordinary pressure. It burns with a bright flame:



When passed into alkaline solutions, it decomposes:



and when heated to 400° it decomposes into its elements.

**Silico-ethane**,  $\text{Si}_2\text{H}_6$ , can be obtained as a liquid by fractionation of the residues from the preparation of silico-methane from magnesium silicide but is better made from the corresponding chlorine compound,  $\text{Si}_2\text{Cl}_6$ , and lithium aluminium hydride. It is a colourless liquid, b.p.  $-15^\circ$ . It decomposes into its elements when heated to 200° in absence of air; in air it is spontaneously inflammable.

#### Silicon Carbide, Carbon Silicide, "Carborundum," $\text{SiC}$

This compound is made by fusing a mixture of coke and sand in an electric resistance furnace—estimated temperature 3500°. The furnace is a large rectangular box with permanent ends and temporary sides. Large carbon electrodes are fitted into the two ends, and project into the furnace. Granulated coke is packed between the electrodes. A mixture of sand and coke, with some salt to make the mass fusible, and some sawdust to make the mass porous, is packed about the carbon core and held in place by the side walls of loosely packed bricks. A powerful current of electricity is sent through the charge. The change which takes place is represented by the symbols:



The carbon monoxide burns above the furnace.

The operation is over in about eight hours. The furnace is then allowed to cool; the side walls are removed, and the silicon carbide removed. The best grades are found nearest the core. The product is crushed and treated with sulphuric acid to remove impurities; it is then washed, dried, and graded according to size.

Silicon carbide crystallizes in hexagonal plates when pure; it may be transparent and colourless, or vary in tint from emerald green to brown or black. The latter varieties are most common. The specific gravity is 3.2. It is not attacked by acids—even hydrofluoric acid. It is decomposed by fusion with alkaline hydroxides. It is nearly as hard as the diamond, and accordingly, known by the trade name of *carborundum*, it is largely used as an abrasive powder and made into whetstones, hones, grinding wheels, polishing cloths, etc. It is used for crucibles for melting metals since it is very refractory and has a much higher heat conductivity than fireclay-graphite (the only other important crucible material used on a large scale). Resistance heaters in the form of carborundum rods are being increasingly used in industrial furnaces.

### § 4 Silica, Silicon Dioxide

Silica is a very common constituent of the earth's crust; some of the ways in which it occurs are mentioned in § 2.

It occurs abundantly in the mineral kingdom, and it is also common in the connective tissue of animals, fibres of vegetables, etc. Bamboo and similar plants contain an unusually high percentage of silica. The so-called *kieselguhr* or "diatomaceous earth" is a friable powder resembling chalk or clay. It is virtually a mass of siliceous skeletons of dead diatoms.

Silica,  $\text{SiO}_2$ , occurs in nature free and combined with various bases to form numerous mineral silicates. Free silica occurs crystalline and amorphous. There are three main types of crystalline silica: quartz, tridymite, and cristobalite; quartz is the most commonly occurring form.

The transition temperatures of these three forms are quartz to tridymite,  $870^\circ$ ; tridymite to cristobalite,  $1470^\circ$ .

Silica is used to a considerable extent as a refractory in furnaces. If the silica of the refractory bricks is in the form of quartz when the furnace is built the change to cristobalite or tridymite when the furnace is in operation will be accompanied by expansion and the splitting of many of the bricks. This phenomenon is known as *spalling*. The bricks are therefore heated before use so as to convert some of the quartz into cristobalite which although metastable below  $1470^\circ$  can exist indefinitely at ordinary temperatures.

### Quartz

Quartz occurs in hexagonal prisms (trigonal system) terminating in hexagonal pyramids. A single quartz crystal weighing very nearly one ton has been reported from Calaveras (U.S.A.). The purest varieties of quartz—called *rock crystal*—are colourless; they have a specific gravity 2.651, and are hard enough to cut glass. The crystals are sometimes coloured with traces of various oxides. Thus, manganese oxide gives *amethyst quartz*; *smoky quartz* probably owes its colour to the presence of carbonaceous matter; *milky quartz* owes its opacity to the presence of innumerable air bubbles. Quartz also occurs massive in quartzite and quartzose rocks. Quartzose sands and sandstones are also more or less impure quartz.

### Amorphous Silica

Amorphous silica occurs in nature associated with 3 to 12 per cent of water in the mineral *opal*, which may be colourless or tinted yellowish brown, etc., with iron oxide, organic matter, etc. Chert, flint, chalcedony, and jasper contain more or less amorphous silica associated with quartz. The silica of diatomaceous earth is opaline and soluble in alkaline carbonate solutions, although the silica in some of the older deposits has begun to crystallize as quartz.

Pure silica is now manufactured by the hydrolysis of silicon tetrachloride (page 781).

### Properties of Silica

Silica melts to a colourless glass—**quartz glass**—in the oxyhydrogen blowpipe. The melting point of quartz is  $1728^\circ$ . Silica can be vaporized in the electric furnace; it boils at  $2230^\circ$ . The specific gravity of vitreous silica is about 2.22. The coefficient of thermal expansion of vitreous quartz is remarkably small—nearly 0.0000005—so that quartz glass

can be very rapidly cooled without cracking. For instance, quartz glass can be heated red hot in the blowpipe and plunged in cold water without fracture; under the same conditions, ordinary glass—with a coefficient of thermal expansion of 0.000008—would shatter into small fragments. When heated for some time at about 1250°, the vitreous quartz passes into the crystalline condition (tridymite), and it will not then bear the sudden heating and cooling so well.

Silica is reduced by carbon in the electric furnace and forms silicon carbide (carborundum) (q.v.); it is reduced by magnesium to amorphous silicon. Crystalline and vitreous silica appear to be insoluble in water and in all acids except hydrofluoric acid. Fused silica is readily attacked by phosphoric acid and by the alkalis. Crystalline silica is slowly attacked by aqueous solutions of alkaline hydroxides, and carbonates, but the amorphous variety is rapidly attacked. Silica is also attacked by superheated water, and a small quantity may pass into solution. The necessary conditions seem to prevail in deep-seated cavities in the earth. The water rising to the surface is cooled, and the pressure reduced. Some of the dissolved silica is then deposited at the mouth of the spring as a thick jelly. This afterwards changes into a hard white porous mass called *geyserite*. The Great Geyser of Iceland, for instance, is surrounded by a large mound or hillock of silica with a tunnel-like cavity from which the geyser discharges.

Although chemically inactive at ordinary temperatures, silica acts as a powerful acid anhydride at high temperatures, combining with bases and many metallic oxides to form more or less fusible silicates. When silica is fused with sodium carbonate, the carbon dioxide is expelled with effervescence.

The more fusible silicates—e.g., lead silicate—are used in making glasses and pottery glazes. Potassium and sodium silicates are soluble in water, and the aqueous solution is sold as **water glass**, and the solid as **soluble glass**. The market demand for *water glass* in Great Britain is not far short of 1,000 tons a day as solution.

Its uses are numerous, depending on the ratio of  $\text{Na}_2\text{O} : \text{SiO}_2$ . Vail is the author of the definitive work on soluble silicates. Summarizing, it can be said that anything from the meta-silicate through the ortho- to the disilicate is a well-defined compound; that up to about  $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$  the silicates find use as detergent adjuvants with very good cleaning and suspending properties; from about 2.5 to 4.0  $\text{SiO}_2$  they are adhesives much used in the box trade, for sticking plywood, and so on. The adhesive properties, which became marked at c. 3.3  $\text{SiO}_2$ , depend on the sudden kink in the viscosity-concentration curve which has interesting theoretical implications such as the formation of miscelles of giant molecules that, at a certain concentration, suddenly start to get orientated.

By and large, detergent uses account for about half the sales of sodium silicate. Other uses are for concrete waterproofing, factitious building materials, pottery (glazes), and clay (flotation), the chemical

trade (including catalyst manufacture), and adhesives for board-making, etc.

The powerful acid character of silica at high temperatures turns on the fact that most of the acid anhydrides— $\text{SO}_3$ ,  $\text{P}_2\text{O}_5$ , etc.—volatilize at much lower temperatures, and consequently, as soon as ever so little, say, sulphur trioxide is displaced, the volatile anhydride passes away and ceases to compete with the silica for the base. At lower temperatures, sulphur trioxide rapidly displaces silica from the bases when competing under equal conditions.

### Uses of Silica

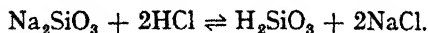
In 1839 M. A. Gaudin showed that quartz can be melted and then worked like glass, but the fact attracted no particular attention until comparatively recent years. Quartz glass is used for the manufacture of elastic threads to suspend the delicate parts of electrical instruments. It is made into tubes, flasks, dishes, etc. Sandstone and quartzite are used for building stones, grindstones, whetstones, etc. Sand or sandstone is ground with a little lime or binding clay and made into refractory bricks, etc. Many varieties of quartz are shaped into ornaments and gems. Diatomaceous earth—also called *tripoli*, *diatomite*, *kieselguhr*, or (wrongly) *infusorial earth*, etc.—is used as a polishing powder, in the manufacture of cement, soluble glass, and heat-insulating bricks. Its absorbent properties are utilized in pharmacy for the preparations of solids saturated with liquid (e.g., antiseptics for dry dressings for wounds) and for the absorption of bromine, sulphuric acid, nitroglycerol, etc. The product when nitroglycerol is absorbed in kieselguhr is known as *dynamite*.

Sand is very extensively employed in building, both for concrete and mortar, also for the manufacture of artificial stone, of glass and glazes, and of silica bricks used in steel and other furnaces. It is also used in the filter beds of waterworks for the purification of public supplies.

### § 5 The Silicic Acids

The substances called silicic acids are rather indefinite compounds, and it is not certain which, if any, of them have a definite existence. But many silicates are known, derived from various (possibly hypothetical) silicic acids.

When a solution of water glass (sodium silicate,  $\text{Na}_2\text{SiO}_3$ ) is acidified with hydrochloric acid, some of the silicic acid separates as a gelatinous mass (hydrogel) and some remains in solution (hydrosol). If the solution be sufficiently dilute, the silicic acid will all remain in solution along with the excess of hydrochloric acid and the sodium chloride formed in the reaction:



The hydrochloric acid and the sodium chloride can be separated from the silicic acid by dialysis (page 278).

A clear solution containing 5 per cent of colloidal silica can be obtained as a hydrosol by dialysis. This solution can be concentrated by boiling in a flask until it contains about 14 per cent of silicic acid. The solution so prepared gelatinizes, or assumes the hydrogel condition, on standing a few days. The passage of silicic acid from the sol to the gel condition is retarded by the presence of a little hydrochloric acid, or alkali hydroxide, and is accelerated by a little sodium carbonate. If the clear solution of silicic acid be allowed to evaporate *in vacuo* at about 15°, a clear transparent jelly is obtained which, when dried over sulphuric acid, has approximately the composition  $\text{H}_2\text{SiO}_2$ , that is,  $\text{SiO}_2 \cdot \text{H}_2\text{O}$ , and it is called **metasilicic acid**. An acid of the same composition has been made by dehydrating gelatinous silicic acid with 90 to 95 per cent of alcohol. An acid of approximately the composition  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , that is,  $\text{H}_4\text{SiO}_4$ , and called **orthosilicic acid**, has been made by dehydrating gelatinous silicic acid with absolute ether, and drying the amorphous white powder between folds of filter paper; the same compound is said to be formed by the action of silicon tetrachloride on water. Orthosilicic acid loses water on exposure to the air. Several other silicic acids have been described, e.g., silico-oxalic acid,  $\text{HO} \cdot \text{OSi} - \text{SiO} \cdot \text{OH}$ ; silico-mesoxalic acid,  $\text{Si}_3\text{O}_2(\text{OH})_4$ .

The formation of metallic silicates is well illustrated by a familiar experiment—*silica garden*. A large beaker is filled with a solution of sodium silicate (sp. gr. 1.1) and crystals of, say, cobalt nitrate, cadmium nitrate, copper sulphate, ferrous sulphate, nickel sulphate, manganese sulphate, zinc sulphate, etc., are allowed to fall into the beaker so as to rest on different parts of the bottom. The whole is allowed to stand overnight in a quiet place, when plant-like shoots appear to grow from the crystals, which have a form and colour characteristic of the metal used as “seed.”

### Silica Gel

If a solution of sodium silicate be heated to 100° and decomposed by hydrochloric acid, a gelatinous precipitate, known as silica gel,  $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ , is obtained. It is also obtained by the action of sodium hydrogen sulphate on sodium silicate solution. This substance has a remarkable power of absorbing moisture, and it is widely used, both in the laboratory and in industry, for drying gases; it has been used for drying the blast in the smelting of iron (page 904). It can also adsorb substances from solution and has been applied to the purification of petroleum products from sulphur.

## § 6 The Silicates

The importance of the silicates, comprising, as they do, so large a proportion of the earth's crust, makes the investigation of their constitution a matter of great interest. They are difficult to investigate by chemical methods, since the majority of them appear to exist only in

the solid state, and the character of the constituent groups is entirely lost in the course of chemical processes. To avoid hypotheses, the silicate industries usually employ the old system of J. J. Berzelius for the empirical formulae, thus writing potash felspar, for example,  $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ , and so on.

Formerly, silicates were classified for chemical purposes on the basis of a series of hypothetical silicic acids.

More recently, it has been shown by means of X-ray analysis, chiefly by W. L. Bragg and by Pauling, that the difference between the different classes of silicates is a matter of the silicon-oxygen arrangement and only indirectly of the remainder of the structures. Occasionally, the silicon-oxygen structure forms a closed group like an ordinary acid radical, but usually the structure is endless and extends continuously throughout a given crystal forming "giant molecules."

The silicon atom in the silicates is always associated with four oxygen atoms, tetrahedrally arranged with regard to the silicon. The way in which these tetrahedral groups are related determines the structure of the particular silicate. Some of these possibilities are indicated in the formulae of Figs 34.1 to 34.3.

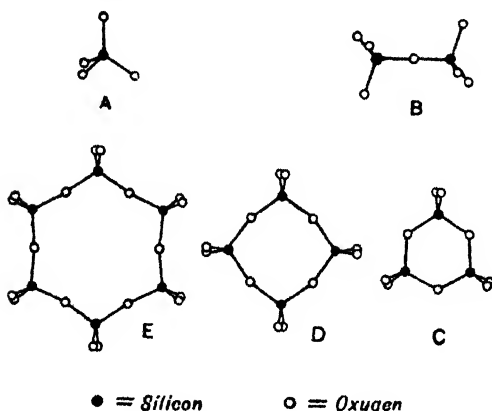


Fig. 34.1 —Silicate Structures: 1

In the orthosilicate group exemplified by *olivine* ( $Mg, Fe$ ) $_2SiO_4$  and *zircon*,  $ZrSiO_4$ , the tetrahedral groups are independent like quadri-valent acid radicals. The oxygen atoms each have one negative charge (being attached to the silicon by a single "valency") and these negative charges attract the metallic ions of the crystal. This represents the simplest silicate type. (Fig. 34.1A)

It is possible for these tetrahedral groups to become linked by their corners, that is, through two groups sharing one oxygen atom.

If two tetrahedra are linked in this way by a single

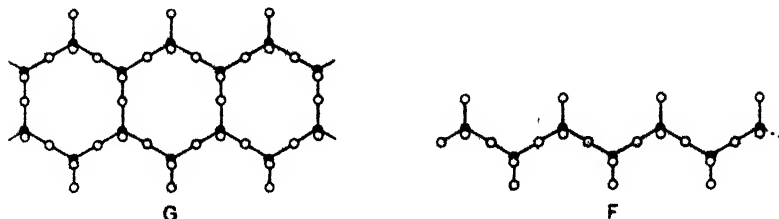
corner of each, a grouping ( $Si_2O_7$ ) results the effective valency of which is six, since the linking oxygen atom now has no charge (Fig. 34.1B). Other groups have been observed in which three tetrahedra are united into a ring through the sharing of three oxygen atoms, thus forming a group ( $Si_3O_8$ ) whose effective valency is again six (Fig. 34.1C). Similarly rings of six such tetrahedra have been found (Fig. 34.1E). Examples of these are the rare mineral *benitoite*,  $BaTiSi_3O_{10}$ , and *beryl*  $Be_3Al_2Si_6O_{18}$ , respectively. A ring composed of four tetrahedra (Fig. 34.1D) has also been detected in certain zeolites.

The process of linking the silicon-oxygen tetrahedra can be continued in long chains and bands such as are found in the pyroxenes and amphiboles respectively. In the chains the tetrahedra are joined corner to corner in a row which extends indefinitely in both directions (Fig. 34.2F). In the crystal there are thus silicon



oxygen structures extending right across the crystal and bound sideways by the positive ions.

In the banded structure of the amphiboles, two of these chains are bound together by the sharing of certain oxygen atoms as indicated in Fig. 34.2g. It is interesting to note that in these two classes of silicate minerals a fibrous structure is exhibited, as for example in asbestos.



F. Chain Structure. G. Band Structure

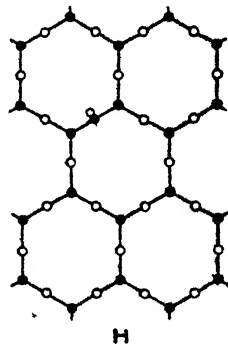
FIG. 34.2.—Silicate Structures: II

A further extension of this process of linking tetrahedra, in which three corners of each are united, results in the formation of sheets. The simplest and most usual arrangement in these sheets is a hexagonal network resulting from the indefinite extension in a second direction of the process by which chains are bound into bands as above. This is indicated in Fig. 34.3H. Here each silicon-oxygen tetrahedron has three shared and only one free oxygen atom. This is the type of structure found in minerals like *mica* and *talc* which are characterized by the ease with which they can be separated into thin leaves. Other ways of forming sheets, as, for example, by the production of rings of four and eight tetrahedra, are also theoretically possible and some of these occur in minerals, though they are not common.

If three-dimensional networks be formed, the tetrahedra are linked by all three corners so that there are no oxygen atoms left carrying charges to attract positive ions. The result is then one of the forms of silica itself (e.g., quartz). In most of the structures already considered a certain number of the silicon atoms may be replaced by aluminium. Whenever this occurs each tetrahedral unit of the framework acquires a resultant negative charge, on account of the lower valency (fewer outer-ring electrons) of aluminium, and metallic ions are then incorporated into the interstices of the structure. The feldspars are examples of this arrangement.

The silicates thus, for the most part, form crystals which are not to be thought of as loose aggregations of "simple" molecules but as *giant-molecules* in which the whole mass is bound by chemical linkages, which extend to the limits of the crystal. The infusibility and insolubility of the silicates is presumably the result of these structures.

The feldspar framework is thus fairly compact but that of the zeolites is relatively open providing channels and holes which accounts for their power of absorbing gases and liquids and the fact that ions can diffuse into these spaces enables them to effect water-softening by ion-exchange (cf. permutit, page 311).



H. Sheet Structure

FIG. 34.3.

Silicate Structures. III

### Weathering of Rocks

Rocks generally show striking differences in behaviour when exposed for long periods of time; some remain hard and firm, others crumble to powder in a comparatively short time. Many ancient Egyptian and Grecian monuments show but slight symptoms of decay, whereas in other countries buildings made from apparently similar rocks soon deteriorate and are saved from disintegration only by a continued system of renovation. Calcareous building stones—e.g., the Houses of Parliament (London)—decay comparatively quickly when exposed to the acidic vapours which occur in the atmospheres of towns. When potash felspar and many other natural alumino-silicates are exposed to certain natural influences, they are finally converted into insoluble white crystalline or amorphous (colloidal) powder—clay, and other materials.

### Formation of Clays

The early stages of the decomposition—weathering—of the felspathic rocks is indicated by the apparent clouding of the crystals of felspar; the felspar becomes more and more opaque, and finally disintegrates. The decomposition of silicate rocks exposed to weathering agents apparently furnishes colloidal silica—e.g., opal—and one of the last stages in the decomposition of felspar, and many other alumino-silicates, is clay. Consequently, the **weathering of the alumino-silicates furnishes clay** in a more or less colloidal condition. Granitic rocks, with felspar as a matrix, disintegrate and leave behind the clay mixed with the more or less resistant varieties of mica, quartz, and other minerals which originally formed the granitic rock. The more important agents which facilitate the decomposition and disintegration—weathering—of the alumino-silicates are: (1) Volcanic gases (steam, hydrofluoric acid vapours, etc.). (2) Water draining from peat bogs and coal beds. This water contains organic acids in solution. (3) Spring or rain water containing carbon dioxide, etc., in solution. The bases derived from the decomposition of the rocks are partly retained by the soil, and partly transformed into carbonates; the silicic acid is partly carried to the sea where it is utilized for building up the skeletons of various organisms, and partly retained on land where it unites with basic minerals forming steatite, serpentine, etc. The clay may be leached by streams of water from the place where it was formed, transported from the hills, and deposited at lower levels. All kinds of debris from the rocks and soils, etc., over which the clays are carried may be transported along with the clay.

Transported clays are usually, but not always, less pure than the residual primary clays. The residual clays formed by the weathering of the less ferruginous granitic rocks, after an elaborate process of washing and settling, furnish white *china clay*, which has very nearly the empirical composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . China clay is often

called "kaolin," generally outside the industry. The disintegrated granite from which china clay is washed is called *china clay rock*; a less disintegrated variety with more unweathered felspar is called *Cornish stone*. The object of washing the china clay rock is to separate the china clay from the unweathered quartz, mica, etc.

The term *clay* is applied industrially to a fine-grained mixture of various minerals which has these qualities: (1) It is plastic enough to be moulded when it is wet; (2) it retains its shape when dried in spite of a certain amount of contraction; and (3) when the moulded mass is heated to a high enough temperature it sinters together, forming a hard coherent mass without losing its original contour. These properties have given clays a most important place—probably third or fourth—in the world's industries. Clays are used in the manufacture of building bricks, tiles, firebricks, crucibles, gas retorts, sanitary goods, pottery, etc.; china clay is also extensively employed for filling paper, cotton, etc. *Fuller's earth* is a kind of non-plastic clay which disintegrates to a fine powder when placed in water. The washed powder was once used for "fulling" cloth—hence the name. It is now largely used for clarifying and deodorizing oils, etc. In this respect, it behaves like charcoal on coloured solutions.

### Pottery and Bricks

British pottery is generally made from an intimate mixture of white-burning clay, with flint or quartz, and felspar or Cornish stone. The mixture is made into a slip (slurry) with water; sieved; and partly de-watered by filter press or other convenient method, so as to form a plastic mass. The mixture is moulded into the desired shape, dried, and fired between 1000° and 1200° according to the kind of ware being made. This forms the so-called "biscuit body." A fusible mixture—containing lead boro-silicate, clay, felspar, etc., ground together to form a "slip" with water—is then spread over the surface of the "biscuit body," and the whole is refired to 900° or 1000°. The melted mixture covers the surface of the "body" with a glassy film or "glaze." There are many modifications. The ware may be decorated by painting coloured oxides on the biscuit body before glazing; or by painting fusible enamels on the glaze and refiring; or the glaze itself may be coloured with suitable oxides. Glaze and body may be fired in one operation with or without a preliminary baking of the body. There are also considerable variations in the composition of the body and glaze. The chief varieties of pottery are *earthenware*—made from white-burning clays, Cornish stone, and flint; *vitreous ware*, and *iron-stone*—made from a similar mixture but containing more fluxes and fired at a higher temperature; *hard porcelain*—made from clays, felspar, and quartz—with or without a little lime; *bone china*—made from bone ash, clay, and Cornish stone; *soft porcelain*—made from a calcareous marl and glassy frit; *parians*—made from a mixture of felspar and clay; and the commoner varieties of pottery—*terra-cotta*

*ware*, etc.—made from special mixtures—often local clays glazed with a mixture containing galena, etc. There are all grades of porosity varying by insensible gradations from translucent glassy porcelain to the most porous terra-cotta. No satisfactory basis of classification has been devised. *Drain pipes* are also made from local clays, which burn a buff or red colour, and glazed by throwing salt into the kiln. The salt decrepitates, volatilizes, and the vapours attack the surface of the clayware, covering it with a glass-like skin—*salt glaze*. *Tobacco pipes* (unglazed) are made from siliceous clays, that is, from clays containing more or less finely divided silica. *Firebricks* are made from refractory clays which soften at about 1580°. The refractory clay is moulded by hand or machinery, and fired to about 1100°–1200°. Common *building bricks* are usually made from less refractory clays fired at a low temperature.

### Ultramarine

Ultramarine or *lapis lazuli*—the sapphire of the Bible—occurs in nature as a blue, green, or violet-coloured mixture of crystalline minerals, the most important of which is *lazurite* (not *lazulite*). It is considered to be a silicate of aluminium and sodium with some combined sulphur; but its constitution is by no means understood. Artificial ultramarine is a blue pigment made by calcining a mixture of china clay, sodium carbonate, charcoal, and sulphur in the absence of air. The green product is washed with water, dried, mixed with sulphur, and again roasted in air until the mass has acquired the required tint. Ultramarine is decomposed by acids with the evolution of hydrogen sulphide. It is used (known commercially as “blue”) for neutralizing the yellowish tinge of sugar, cotton and linen goods, and in the laundry. It is also used as a blue pigment. The mineral has been almost superseded by the artificial product which is but one-fifth the price. Ultramarine is essentially a zeolite but contains negative ions such as  $\text{SO}_4^{--}$ ,  $\text{S}^{--}$  and polysulphide ions. The origin of the colour has often been ascribed to the presence of colloidal sulphur; more recently it has been suggested that it is caused, in some manner not entirely understood, by the inclusion of polysulphide ions in the structure.

### Glass

Glass is a congealed or solidified, undercooled solution of several silicates—most commonly potassium, calcium, and lead—and is made by fusing together a mixture of clean sand, limestone, or whiting or lime, sodium carbonate (or sulphate) or potassium carbonate, and litharge or red lead in the right proportions. Traces of manganese dioxide or selenium are sometimes added to neutralize the yellow or green tinge due to the presence of ferrous or ferric oxide present as impurity in the ingredients used in making the glass. The mixture is melted in fireclay pots, and when the molten mass has cooled to the

right temperature it can be poured into moulds, rolled into sheets, moulded with dies or drawn into rods and tubes or blown into a variety of shapes. The industry is now highly mechanized; large machines are in use for the production of such things as glass bottles, electric lamp globes in great numbers automatically. Rapidly cooled glass is brittle and liable to fracture, hence the glass is annealed in an annealing kiln where it can be cooled as slowly as desired. If cooled too slowly the glass devitrifies, i.e., crystallizes.

It has been said that "few substances in daily use can be compared with glass in point of importance or utility. Glass is so common and so cheap that we are apt to lose sight of its unique qualities. It is durable, transparent, and easily cleaned; it can be readily coloured with metallic oxides; it is capable of taking a high polish; and, while in a fused condition, it can be made to assume almost any desired shape which it retains permanently when cold. It is an indispensable agent in most of the experimental sciences—chemistry, physics, astronomy, etc.—and it is difficult to imagine how many operations could be carried on without its aid. Without glass we should be more than centuries behind in astronomy, bacteriology, and biology." Window glass is a soda-lime silicate. This type of glass is sometimes called "soda-glass" or "soft glass," and it is used for making chemical glass ware. *Window glass*, *plate glass*, and glass for table ware and bottles are also made from the same constituents in different proportions and of different degrees of purity. *Bohemian glass* is a potash-lime silicate. It is a hard glass and fuses only at a high temperature, hence it is used for making chemical apparatus designed to withstand high temperatures: gauge-tubes for boilers, etc. It also resists the solvent action of water better than soda-glass. *Jena glass* is a variety of potash-lime glass. *Flint glass* is a lead-potash silicate. It is lustrous, and refracts light much better than other types of glass. It is used for making lenses for optical purposes. Some varieties are made into artificial gems and ornamental glass. *Cut glass* is a variety of lead glass which is ground or "cut" on emery or carborundum wheels. Beside these special admixtures, metallic oxides may be added to colour the glass. Translucent or white glass is made by the addition of bone ash, or fluorspar, or cryolite. Boric acid is also used in the manufacture of glass with a high refractive index for optical purposes and for certain kinds of chemical apparatus, known as boro-silicate glass.

Of recent years glass containing a high percentage of silica (e.g., Pyrex, Monax) and which, in consequence, is very resistant to heat (and to sudden changes of temperature), has come into increasing use both for laboratory and oven ware. Pyrex glass, for example, contains approximately 80 per cent of silica.

### § 7 Silicon Halides

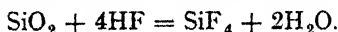
Silicon forms a number of compounds with the halogens of which the most important are:

Silicon tetrafluoride,  $\text{SiF}_4$ ,  
and Silicon tetrachloride,  $\text{SiCl}_4$ .

Of the others, silicon hexachloride,  $\text{Si}_2\text{Cl}_6$ , silico-chloroform,  $\text{SiHCl}_3$ , and compounds of the formulae  $\text{Si}_2\text{F}_6$ ,  $\text{Si}_3\text{Cl}_8$ ,  $\text{SiBr}_4$ ,  $\text{Si}_2\text{Br}_6$ ,  $\text{SiHBr}_3$ ,  $\text{SiI}_4$ ,  $\text{Si}_2\text{I}_6$ ,  $\text{SiHI}_3$ , have been described, as well as several oxychlorides.

#### Silicon Tetrafluoride, or Tetrafluosilicomethane, $\text{SiF}_4$

This gaseous compound is important. It was discovered by K. W. Scheele in 1771. It was afterwards made by J. Priestley, and its composition determined by J. L. Gay-Lussac and J. Thénard, 1808; J. Davy, 1812; and J. J. Berzelius, 1824. Silicon tetrafluoride is made by the direct action of fluorine on amorphous silicon, and also by the action of hydrofluoric acid upon silica or on a silicate—e.g., glass:



Silicon tetrafluoride is usually made by the action of hydrofluoric acid derived from a mixture of calcium fluoride and sulphuric acid upon silica. The mixture is heated in a flask—illustrated in Fig. 34.4—fitted with a safety funnel containing mercury. An excess of sulphuric acid is used to absorb the water formed during the reaction. Another convenient method is by dissolving silica in concentrated aqueous hydrofluoric acid and adding the solution which results to concentrated sulphuric acid.

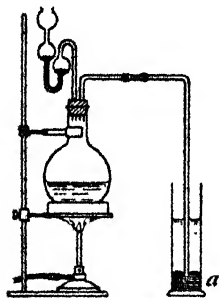
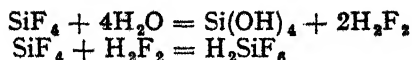


FIG. 34.4.—Preparation of Hydrofluosilicic Acid

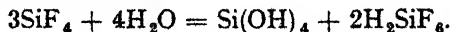
Silicon tetrafluoride is a colourless gas with a pungent odour resembling hydrogen chloride. The density of the gas corresponds with the formula  $\text{SiF}_4$ . Silicon tetrafluoride condenses to a colourless liquid which boils at  $-77^\circ$ ; it forms a white solid which melts at  $-65^\circ$ . It can be sublimed without liquefaction at  $-90^\circ$  at ordinary pressures. Glass is not attacked by dry silicon tetrafluoride.

#### Hydrofluosilicic acid, $\text{H}_2\text{SiF}_6$

If silicon tetrafluoride be passed into water, it decomposes, gelatinous silicic acid is precipitated, and hydrogen fluoride is formed. The hydrogen fluoride immediately combines with a molecule of silicon tetrafluoride, producing an aqueous solution of hydrofluosilicic acid. The reactions may be written:



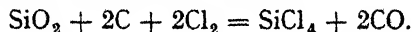
or, combined in one equation,



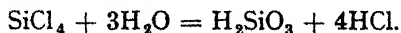
In order to prevent the choking of the delivery tube by the separation of silicic acid when the silicon tetrafluoride is passed into water, it is well to let the delivery tube dip below a little mercury, *a*, Fig. 34.4, placed at the bottom of the vessel of water. The aqueous layer is frequently stirred to prevent the formation of channels of silicic acid through which the gas can escape into the atmosphere without coming in contact with the water. The silicic acid is separated from the aqueous solution by filtration; the aqueous solution cannot be concentrated very much by evaporation because it decomposes into silicon tetrafluoride and hydrogen fluoride; pure hydrofluosilicic acid is not known.

Hydrofluosilicic acid reddens blue litmus, and it is neutralized by the bases forming salts, **fluosilicates**. Most of the fluosilicates are fairly soluble in water, but the potassium and barium fluosilicates are sparingly soluble. Hence the use of hydrofluosilicic acid in testing for barium salts, and in the estimation of potassium. Hydrofluosilicic acid is used for giving wood a stone-like surface. The wood is first soaked in lime water and then treated with hydrofluosilicic acid. The acid is also used as an antiseptic in medicine.

**Silicon tetrachloride, tetrachlorosilicomethane**,  $\text{SiCl}_4$ , can be made by heating silicon, ferrosilicon, silicon carbide, or an intimate mixture of carbon and silica in a stream of chlorine:



The liquid which condenses can be freed from the excess of chlorine by shaking it with mercury, and redistilling. The colourless fuming liquid so obtained fumes in moist air. It has a vapour density and composition corresponding with  $\text{SiCl}_4$ . Silicon tetrachloride boils at  $59.6^\circ$  and freezes at  $-70^\circ$ ; carbon tetrachloride boils at  $76.8^\circ$  and freezes at  $-22^\circ$ . Silicon tetrachloride is decomposed by water into silicic and hydrochloric acids:



This behaviour is in marked contrast to that of carbon tetrachloride (page 407) which does not react with water. This is explained as a consequence of the co-valency maximum for carbon being four, while for silicon it is six, so that water can attach itself to the silicon atom of silicon tetrachloride (the oxygen acting as donor). A hydrogen atom from the water and a chlorine atom from the chloride are then eliminated, the position occupied by the chlorine being taken by a hydroxyl group. This process can then be repeated until hydrolysis is complete. But the carbon atom cannot attach a water molecule since it has already reached its maximum covalency; consequently no hydrolysis occurs.

Silicon tetrachloride finds commercial application in the manufacture of pure silica, of esters of silicic acid and of silicones.

### § 8 Germanium, Ge

Germanium was discovered in 1886 by Winkler in a silver mineral *argyrodite* from Saxony, as a result of an apparent discrepancy in the results of his analysis of this mineral. For long germanium was very rare and no more than a chemical curiosity, but during the last few years it has been found in certain coals, in which it occurs along with gallium (page 753). It can be recovered from the ash, or better, from the flue dust from waste-heat boilers or from the producers used for heating the retorts in gasworks. The mineral *germanite*, discovered in S.W. Africa in 1916, contains up to 5 per cent of the element. Germanium is the eka-silicon of Mendeleeff (cf. page 131). Germanium has now become important for its property of semi-conductivity which has led to its use in transistors; experiments are proceeding on its application also to the rectification of alternating current for traction purposes; an experimental train, equipped with a germanium rectifier, is already in use in Lancashire.

Germanium is extracted from the ash, or flue dust, by smelting it along with a copper ore so as to obtain a matte, or regulus, which contains copper, iron, germanium and gallium along with sulphur or arsenic. By heating this in a stream of chlorine, arsenic trichloride and germanic chloride are formed and are volatilized off; they are then separated by fractional distillation and the metallic germanium is obtained by reduction of the chloride with hydrogen. For use in transistors very pure germanium is necessary; the final purification is effected by the newly developed process of "zone melting" or "zone refining." This involves the heating of a strip of metal in such a way that a zone of fusion passes along it from one end to the other; the impurities eventually collect in the melted zone at the end of the strip, which is removed and reworked.

Germanium is a greyish-white, brittle metal which gives rise to two series of compounds in which it is respectively bi- and quadrivalent. As well as its use as a rectifier it is also used, in the form of magnesium germanate, in fluorescent discharge lamps in which it gives rise to a red fluorescence which helps to correct the colour balance of the light emitted.

The compounds corresponding with bivalent germanium, being covalent, resemble those of silicon and carbon, and compounds corresponding with quadrivalent germanium resemble tin and titanium compounds. The analysis and vapour density of germanium tetrachloride correspond with an atomic weight 72.6 (oxygen = 16). This number agrees roughly with the atomic weight calculated from the specific heat 0.08 by Dulong and Petit's rule.

### § 9 Tin, Sn

#### History

Discoveries of tin in Egyptian tombs show that the metal was fairly common in olden times. It is not certain if the Hebrew word "bedil" in the Pentateuch, translated by the Greek word *κασσίτερος* (*cassiteros*), and by the Latin word *stannum*, really means tin. The word "stannum" appears to have been used by the Romans to designate certain alloys containing lead. It is not certain whether the Phoenicians obtained their tin from the East, Britain, or Iberia. The resemblance between the Sanscrit word "castira" and the Greek "cassiteros" has been used as an argument in favour of the Eastern origin of Phoenician tin. Pliny states that "cassiteron" was obtained from "Cassiterides in the Atlantic Ocean." This no doubt refers to the tin then obtained from the Cornish mines, for "certain islands north of Spain" were often referred to as the *insulae cassiterides*—tin islands.



The Romans appear to have distinguished lead from tin by calling lead "plumbum nigrum," and tin "plumbum candidum." The word "stannum" was later restricted to tin proper.

### Occurrence

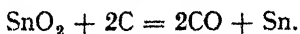
There are several reports of the occurrence of metallic tin in nature—in Bohemia, Bolivia, New South Wales, Nigeria—but *tinstone* or *cassiterite* is the sole source of commercial tin. This mineral occurs in tetragonal crystals coloured brown or black by impurities, chiefly iron. Cassiterite is stannic oxide,  $\text{SnO}_2$ , contaminated with more or less arsenical pyrites, copper pyrites, tungstates, and various metallic sulphides. *Lode tin* or *vein tin* is cassiterite which is obtained from veins or lodes in primary deposits; while "stream" tin is cassiterite from alluvial secondary deposits where it occurs in more or less rounded lumps. The miners speak of tinstone as "tin" or *black tin* to distinguish it from the metal which is called *white tin*. The complex sulphide ore, *stannite*, or *tin pyrites*, is a sulphide of copper, tin, iron, and sometimes zinc. It is comparatively rare. About one-third of the world's output of tin is produced in the Malay peninsula, which furnishes the so-called *Straits tin*. Tin is also produced in the Malay archipelago (e.g., at Banca), in Bolivia, Nigeria, Australia, Cornwall, South Africa, Bohemia, and Saxony.

It is noteworthy that tin is less abundant than its extensive use would seem to indicate; it is considerably less abundant, in fact, than titanium, which is often thought of as a scarce element.

### Extraction

The method of extracting tin from its ore, the metallurgy of tin, is comparatively simple, owing, no doubt, to the simplicity of the ore—black tin. The ore is first concentrated by washing away the earthy impurities. The high specific gravity of tinstone—6.8 to 7.0—enables this to be done without much trouble, as in the case of washing gold (cf. page 674). This process usually works well with stream tin; but vein tin usually requires more complex treatment. The crushed ore is first washed to remove earthy matters. The arsenic and sulphur are removed by an "oxidizing roast." The tungsten and the residue left after the calcination of the pyrites are removed by passing the calcined ore through the intense magnetic field of an "electro-magnetic separator."

The extraction of tin from the concentrates, as they are called, involves reduction of the "concentrated" ore—tinstone—by heating it with coke or coal and limestone in either a reverberatory furnace or a small blast furnace. The oxide is reduced:



The molten tin which collects on the bottom of the furnace is drawn off and cast into ingots or blocks—block tin—which contain about

99.5 per cent of metallic tin. The slag obtained in this operation is also worked up to recover the 20 to 40 per cent of metal it contains.

### Refining Tin

Tin is refined by heating it, at a temperature as little as possible above the melting point of the metal, on the sloping hearth of a reverberatory furnace. The tin flows down the hearth and leaves the oxidized metallic impurities as "refinery dross" behind. This tin may be further purified by stirring the molten metal with a billet of wood. The metal is agitated by the bubbling of the rising gases, and this continually exposes fresh portions of the molten metal to the oxidizing action of the air. The impurities which collect on the surface as a "dross" are skimmed off. The refinery drosses containing a large percentage of tin are resmelted with the ore. Electrolytic processes for the refining of tin are being developed; hydrofluosilicic acid and sodium sulphide have been used as electrolytes.

The recovery of tin from old tinplate and other scrap materials is an important process and is carried out by treating the scrap material (after washing with alkali to remove grease, etc., and heating to melt off solder) with chlorine in a closed iron cylinder. Volatile stannic chloride is formed from which metallic tin can be recovered; it is sometimes converted into the hydrate  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , which finds a use in the silk industry, or into ammonium chlorostannate, used as a mordant in dyeing (page 790). The iron scrap remaining is smelted in an open-hearth furnace.

Electrolytic recovery processes are now being developed. The scrap tinplate is made the anode of a cell, using sodium cyanide as electrolyte. Spongy tin is deposited on the steel cathode.

## § 10 Properties of Tin

Tin is a white lustrous metal with a pale blue tinge. The metal retains its lustre unimpaired by exposure to air. The metal is soft enough to be cut with a knife, but it is harder than lead, and not so hard as zinc. Tin is very ductile, for it can be beaten into foil—tin foil—0.01 to 0.1 mm. thick, and drawn into wire. The ductility of tin is greatest at about 100°; at 200° the metal is brittle enough to be powdered. If a bar of tin be bent, it emits a low crackling noise—"tin cry"—said to be caused by the rubbing of the crystal faces upon one another. The density of tin is 7.3 at 20°.

Tin melts at 231.9° and boils at 2337°; a perceptible volatilization occurs at 1200°. Tin exists in three allotropic forms. As ordinarily obtained it forms tetragonal crystals; but the brittle tin mentioned above is rhombic. Tetragonal tin passes into rhombic at about 170°, which is the transition point of the two forms.

When cooled to a low temperature tin crumbles to a grey friable

powder. Several cases have been reported where tin, during an exceptionally cold winter, has crumbled to powder; for instance, A. L. Erdmann (1851) noticed some tin organ-pipes in the church at Zeitz crumbled to powder; and later, the tin buttons of some military uniforms were found to have crumbled to powder while in the depot during a cold winter. The "disease" is called the "tin pest." The afflicted tin first tarnishes, then shows faint radiating formations, and then wart-like formations, and finally the metal crumbles to a grey pulverulent mass. The afflicted metal contains two kinds of tin—the one, ordinary white bright tin; and the other grey, dull, pulverulent tin. Grey tin appears to be a third modification of the element.

The transition temperature is  $18^{\circ}$ . Hence, excepting in warm weather, all ordinary white tin is in a metastable condition; but, as E. Cohen has pointed out, the speed of the transformation is very slow at ordinary temperatures. The transformation proceeds with a maximum velocity at  $-48^{\circ}$ , especially if the tin be in contact with an alcoholic solution of "pink salt,"  $(\text{NH}_4)_2\text{SnCl}_2$ . At lower temperatures, the velocity again slows down. The "disease" is contagious, for if a piece of tin which has already commenced to change be allowed to remain in contact with a piece of ordinary white tin, the unchanged tin is more quickly affected with the "disease."

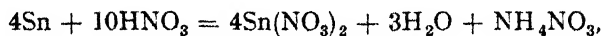
Tin is not attacked either by water or air at ordinary temperatures either separately or together; hence it is used as a protective covering. It takes fire when heated in air to between  $1500^{\circ}$  and  $1600^{\circ}$ , burning with a white flame to stannic oxide. It combines directly with chlorine forming stannic chloride; it reacts slowly with dilute hydrochloric acid and fairly rapidly with the concentrated acid, forming solutions of stannous chloride:



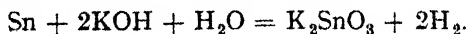
Tin is but slowly attacked by cold sulphuric acid, but the hot, concentrated acid attacks the metal, forming stannic sulphate and sulphur dioxide:



The action of nitric acid depends upon the temperature and concentration of the acid. With cold, very dilute nitric acid, stannous nitrate is formed:



with possibly a little stannic nitrate,  $\text{Sn}(\text{NO}_3)_4$ . With nitric acid of moderate concentration (e.g., sp. gr. 1.24), copious fumes are evolved, and a bulky white precipitate of a hydrated oxide, *metastannic acid*, separates. Highly concentrated or pure nitric acid is almost without action on tin. Boiling concentrated alkali hydroxide solutions slowly attack tin, forming solutions of stannates, e.g.:



### § 11 Uses of Tin

The most extensive use of tin is in the manufacture of tinplate. Thin sheets of iron or mild steel are "pickled" by dipping in dilute acid to remove oxide, etc., and are then passed into a bath of molten tin on the surface of which floats a flux such as rosin, zinc chloride, etc.

Tin is also a constituent of many useful alloys, e.g., solder, pewter, type metal, bronze (page 651), bearing metal, and Britannia metal.

*Plumber's solder* contains about 70 per cent of lead and 30 per cent of tin. This alloy solidifies over a considerable range of temperature during which it is pasty thus enabling a joint to be "wiped."

Ordinary *fine solder* consists of 33 per cent lead and 66 per cent tin; *common solder* contains equal parts of lead and tin. *Pewter* contains 75 per cent of tin and 25 per cent of lead. *Type metal* has 75 per cent of lead, 5 per cent of tin, and 20 per cent of antimony. A typical *bearing metal*, such as is used in locomotives, contains 82 per cent of tin, 14 per cent of antimony and 4 per cent of copper. *Britannia metal*, a somewhat similar alloy, has 93 per cent of tin, 5 per cent of antimony, and 2 per cent of copper.

A white, coarsely crystalline mass known as *phosphor tin* is obtained by adding phosphorus to molten tin. It is used for the manufacture of phosphor-bronze (page 651).

### § 12 Atomic Weight of Tin

The vapour density of the volatile compounds of tin, observations on the isomorphism of stannic and titanous oxides, and the specific heat of tin (0.055) indicate a number round about 119 for the atomic weight.

The exact value of the combining weight has been determined from analysis or synthesis of the oxide, chloride, potassium and ammonium stannichlorides; and by the separation of tin from stannic chloride by electrolysis. The value recommended at present (1957) by the International Committee is 118.7, and is based on the work of Briscoe (1915) who determined the ratio  $\text{SnCl}_4 : 4\text{Ag}$  by breaking bulbs of specially purified stannic chloride in a solution of silver in nitric acid

### § 13 Oxides and Hydroxides of Tin. Stannic Acids

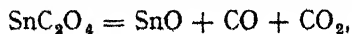
Tin forms two oxides, viz.,

Stannous oxide,  $\text{SnO}$ ,  
Stannic oxide,  $\text{SnO}_2$ ,

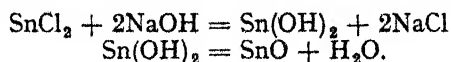
and corresponding to them are two series of tin compounds, the stannous and the stannic.

#### Stannous Oxide, $\text{SnO}$

Stannous oxide can be made by heating stannous oxalate



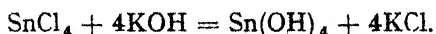
or by careful heating of *stannous hydroxide*,  $\text{Sn}(\text{OH})_2$ , in a stream of carbon dioxide. Stannous hydroxide is precipitated on the addition of alkalis to a solution of stannous chloride (excess being avoided):



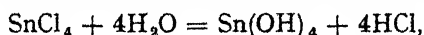
Stannous oxide is a brown or dark-grey powder which burns in air to stannic oxide. It reacts with acids forming stannous salts, and also with alkalis, forming *stannites* which are regarded as salts of stannous acid,  $\text{H}_2\text{SnO}_2$ , i.e., of stannous hydroxide reacting as an acid.

### Stannic Hydroxide

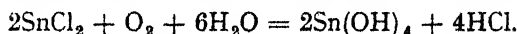
Stannic hydroxide is precipitated by ammonia, alkali hydroxides (not in excess), carbonates, etc., from solutions of stannic salts, e.g.,



It is also formed by hydrolysis of stannic chloride in water:



and when a solution of stannous chloride is exposed to the air. Possibly, in this case, stannic chloride is first formed and then hydrolysed:



If the precipitate obtained in these ways be dried in air, it has the empirical composition  $\text{H}_4\text{SnO}_4$  or  $\text{Sn}(\text{OH})_4$ ; and if dried over concentrated sulphuric acid, the empirical composition is  $\text{H}_2\text{SnO}_3$  or  $\text{SnO} \cdot (\text{OH})_2$ . The former is regarded as **orthostannic acid** and the latter as **metastannic acid**.

Stannates, such as  $\text{K}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ , can be made by heating solutions of stannic chloride and alkali carbonates or hydroxides; from aqueous solutions of these stannates, a metastannic acid,  $\text{H}_2\text{SnO}_3$ , is precipitated by carbon dioxide.

When tin is heated with nitric acid (sp. gr. 1.3), stannic hydroxide is formed which, if dried over sulphuric acid, also has the empirical formula  $\text{H}_2\text{SnO}_3$ . But the stannic acids formed by these two processes differ in their behaviour towards many reagents. For convenience, the acid formed by the action of alkalis on solutions of stannic chloride is called the  $\alpha$ -acid, and that produced by the action of nitric acid on the metal is known as the  $\beta$ -acid. Some of the differences between the two metastannic acids are indicated in Table LI.

Both varieties dissolve in caustic alkalis and alkali carbonates, and when reprecipitated by acids, they are said to retain the properties they had before being so dissolved. If the  $\beta$ -acid be boiled for a long time with concentrated hydrochloric acid, or concentrated alkali hydroxide solution, it is gradually converted into the  $\alpha$ -acid; and, conversely, the  $\alpha$ -acid is gradually changed into the  $\beta$ -acid at ordinary temperatures and more rapidly on boiling with water.

An explanation of the difference between the two acids is not known with certainty; but it is supposed that the  $\beta$ -acid is a polymerized form— $(\text{H}_2\text{SnO}_3)_5$ —of the  $\alpha$ -acid— $\text{H}_2\text{SnO}_3$ .

TABLE LI.—PROPERTIES OF THE METASTANNIC ACIDS

$\alpha$ -Metastannic acid	$\beta$ -Metastannic acid
Salts dissolve in water easily and are not decomposed. More basic than the $\beta$ -acid.	Salts dissolve in water with difficulty and form insoluble basic salts and free acid. Less basic than the $\alpha$ -acid.
When moist, dissolves readily in nitric acid.	Insoluble in nitric acid.
Soluble in dilute sulphuric acid and the solution does not gelatinize when boiled.	Insoluble in sulphuric acid even if concentrated.
Easily soluble in hydrochloric acid and the solution remains clear when boiled.	Unites with hydrochloric acid forming a substance insoluble in acid but soluble in water. The aqueous solution gelatinizes when boiled.

The idea is growing in some quarters that the difference is only one of size of grain and that there are not two definite and distinct acids. It is difficult to reconcile this view, however, with the observation that the differences persist after solution in caustic alkali and reprecipitation.

**Sodium stannate**,  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ , is made commercially by fusing tin with a mixture of caustic soda, sodium nitrate and sodium chloride. It is a white crystalline substance, containing 3 molecules of water, and is used as a mordant in calico-printing under the name of *preparing salts*.

**Stannic oxide**,  $\text{SnO}_2$ , occurs in nature and is the principal ore of tin. It crystallizes in three different forms and is iso-trimorphous with the corresponding titanium compound (q.v.). It is formed by heating tin in air, or by calcining the stannic acids. It is a white powder which is unattacked by acids, except concentrated sulphuric acid, with which it reacts, forming a solution which may contain stannic sulphate,  $\text{Sn}(\text{SO}_4)_2$ . On dilution, the oxide is reprecipitated. It also reacts with solutions of alkali hydroxides, forming stannates:



Stannic oxide is used in making white glazes for tiles, and for milk-glass articles such as electric-light shades.

### § 14 Salts of Tin

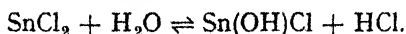
Tin forms two series of salts, corresponding to the two oxides, known as the stannous salts and the stannic salts respectively. Stannic oxide is a very weak base indeed, and in the quadrivalent state tin forms covalent compounds resembling those of a non-metal; e.g., stannic chloride is a liquid, readily hydrolysed by water.

**Stannous Chloride,  $\text{SnCl}_2$** 

Stannous chloride can be prepared by the action of hydrochloric acid on tin; the solution on evaporation deposits monoclinic crystals of the dihydrate,  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , known as *tin salt*. When dried *in vacuo*, the anhydrous salt is formed; the anhydrous salt also results when tin is heated in a stream of hydrogen chloride, and also by heating a mixture of metallic tin and mercuric chloride, when the mercury volatilizes, and the stannous chloride remains:

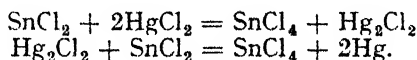


Stannous chloride dissolves in water, without noticeable change, if only a small quantity is used; with excess of water, hydrolysis occurs and a basic chloride is precipitated:

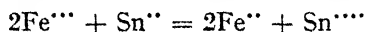


The precipitate redissolves on addition of hydrochloric acid. Solutions of alkali hydroxides precipitate stannous hydroxide which redissolves in excess, forming stannites.

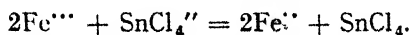
Stannous chloride is a powerful reducing agent, and readily combines with oxygen or chlorine. Thus it reduces mercuric chloride to mercurous chloride and, if the action be allowed to continue, to metallic mercury:



Ferric salts and cupric salts are reduced by stannous chloride to the ferrous and cuprous states respectively. The reduction of metallic ions, such as ferric, is often represented by an equation of the form



but it seems unlikely that this should represent accurately what happens since the large positive charges on both sorts of ions would tend to keep them apart. For this reason, it has been suggested that the effective reducing agent, in such cases, is a complex ion, such as  $\text{SnCl}_4''$ , when the reverse would be true and, for instance, it and the ferric ion would be attracted to each other, being oppositely charged:



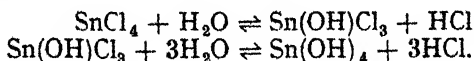
Stannous chloride acts upon nitric acid with the formation of hydroxylamine ( $\text{NH}_2\text{OH}$ ) and it is frequently employed in organic chemistry.

Stannous chloride is used as a mordant in dyeing.

**Stannic Chloride,  $\text{SnCl}_4$** 

This compound is prepared by the action of chlorine on molten metallic tin, the stannic chloride, which is volatile, being collected in a cooled receiver. It is a colourless, fuming liquid which boils at  $114.1^\circ$ ,

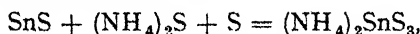
and fumes strongly in moist air. The action of a little moisture converts it into a solid pentahydrate,  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ , known as *oxymuriate of tin* which is used as a mordant. With excess of water, basic chlorides, and ultimately stannic acid, are formed:



Stannic chloride forms a series of complex salts, the most important of which is **ammonium chlorostannate**,  $(\text{NH}_4)_2\text{SnCl}_6$ , used as a mordant under the name of *pink salt*.

### The Sulphides

When tin foil is burned in sulphur vapour, **stannous sulphide**,  $\text{SnS}$ , is formed. It is precipitated as a brown powder when hydrogen sulphide is passed through a solution of a stannous salt. The precipitate becomes black on drying. It is soluble in strongly acid solutions, but is reprecipitated on dilution. It is also soluble in alkali and ammonium polysulphides, forming **thiostannates**, e.g.,



and yellow stannic sulphide is precipitated on acidification. It is insoluble in ammonia, ammonium carbonate and colourless ammonium sulphide.

**Stannic sulphide**,  $\text{SnS}_2$ , is precipitated by passing hydrogen sulphide through a (not too strongly acid) solution of a stannic salt. It dissolves in alkali sulphides, forming the same thiostannates as above. It is insoluble in ammonia and ammonium carbonate.

On heating a mixture of tin amalgam, ammonium chloride and sulphur in a retort, a complex reaction takes place resulting in the formation of a mass of yellow scales of stannic sulphide called *mosaic gold* which is used as a pigment.

## § 15 Detection and Determination of Tin

Tin is usually recognized in qualitative analysis by the precipitation of its sulphides, in acid solution, on passing hydrogen sulphide. They are separated from the sulphides of copper, lead, mercury, bismuth and cadmium by the action of yellow ammonium sulphide, with which they react, forming soluble thiostannates. Arsenic and antimony sulphides behave similarly with this reagent, from which on acidification arsenic and antimony pentasulphides, and stannic sulphide are precipitated. These three may be separated as follows. The arsenic is first removed by adding solid ammonium carbonate and a few drops of water and warming to  $40^\circ$ . After filtering, arsenic pentasulphide is precipitated from the filtrate on addition of dilute hydrochloric acid. The residue (antimony and tin sulphides) after washing with ammonium chloride solution, is warmed to  $80^\circ$  with a little milk of lime. The



antimony pentasulphide is converted into a yellow solution of calcium thioantimonate, while the stannic sulphide becomes hydrated stannic oxide. When the precipitate is all colourless, the solution is filtered; antimony pentasulphide is precipitated on acidification of the filtrate, while the residue, after solution in warm dilute hydrochloric acid, deposits stannic hydroxide as a white gelatinous precipitate on addition of ammonium chloride and ammonia.

Tin is often determined gravimetrically by conversion into stannic oxide by the action of nitric acid followed by ignition. This method is used for alloys, because the other metals present usually form soluble nitrates. The salts are converted to the stannic condition, and then precipitated as stannic hydroxide, which is ignited.

Volumetrically, tin can be determined by means of iodine, provided it is in the stannous condition. The reaction is sometimes expressed:



Stannic salts can be determined if they are first reduced to stannous by, say, iron or nickel in acid solution.

Tin can also be determined by precipitation with "cupferron" ( $\text{C}_8\text{H}_5\text{N}(\text{NO})\text{ONH}_4$ ) by adding a 10 per cent solution to the cold tin solution. It forms a white precipitate which on ignition leaves stannic oxide, which is weighed. Tin can be determined in this way, in presence of aluminium, chromium, cobalt, nickel or manganese, but copper, lead, arsenic, and antimony interfere and so must first be removed.

## § 16 Lead, Pb

### History

Lead was known to the ancient Egyptians. It is mentioned several times in the Old Testament. It appears to have been confused with tin (q.v.), and Pliny seems to have distinguished between *plumbum nigrum* (black lead) and *plumbum album* or *plumbum candidum*. The ancient Romans used lead for making water-pipes, and some lead compounds were used as cosmetics, and as paint.

### Occurrence

Small quantities of metallic lead are occasionally found in nature. In combination with sulphur, lead occurs as the sulphide, *galena*,  $\text{PbS}$ . This is the most abundant ore of lead. Commercial lead is obtained almost exclusively from *galena*. Lead carbonate, *cerussite*,  $\text{PbCO}_3$ , is not uncommon. Lead sulphate, *anglesite*,  $\text{PbSO}_4$ , occurs as *anglesite*; lead chromate, *crocoisite*,  $\text{PbCrO}_4$ ; lead molybdate, *wulfenite*,  $\text{PbMoO}_4$ ; lead phosphate, *pyromorphite*,  $\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{PO}_4)_2$ ; lead chloride, *matlockite*,  $\text{PbCl}_2$ . Lead ores come from England, United States, Germany, Mexico, Spain, New South Wales, South America, etc.

### Extraction

Galena often occurs associated with zinc blende so that it is usually necessary to concentrate the ore before smelting. This is effected either by mechanical washing or by flotation or by a combination of both methods (cf. page 600).

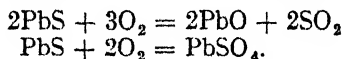
Two main methods are employed for the extraction of lead, viz.:

- (i) reverberatory furnace smelting, and
- (ii) the blast furnace method.

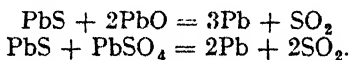
The former was for long the main process but the latter is now coming into increasing use.

The reverberatory furnace process is carried out in two stages, known as the *roasting* stage and the *reaction* stage respectively.

In the roasting stage, the temperature is kept below the melting point of the charge, and air is admitted so that the part of the sulphide is converted into a mixture of oxide and sulphate:



In the reaction stage, a higher temperature is employed, the air supply is cut off, and the charge melts, lead being formed according to the reactions:



For the blast furnace method, the ore is subjected to a preliminary roasting so as to sinter the finely divided ore or concentrate into lumps of suitable size; at the same time most of it is converted into the oxide. This is then mixed with fuel and smelted in a small blast furnace, reduction of the oxide taking place, mainly brought about by carbon and carbon monoxide; but to a lesser extent by any surviving lead sulphide.

The lead obtained by these processes usually contains small amounts of antimony, tin, copper, etc., which make it hard and brittle, as well as silver in quantity sufficient to make recovery profitable. Most of the impurities can be removed by heating the metal in a shallow, flat-bottomed, reverberatory furnace, whereby they are oxidized before the lead and rise to the surface as a scum which is skimmed off. Electrolytic methods are now being applied to the refining of lead; a bath of lead fluosilicate containing some free hydrofluosilicic acid being used (Bett's process). The silver is usually extracted by Parkes's process (page 665).

### § 17 Properties of Lead

Lead is a bluish-grey metal with a bright metallic lustre when freshly cut, but the lustre soon disappears in ordinary air. Perfectly dry air, and air-free water, have no action on the metal, but if moist

air be present, or if the metal be immersed in aerated water, lead is soon covered with a film, probably an oxide, and this is ultimately converted into a basic carbonate. Lead is soft enough to be cut with a knife and scratched with the finger nail. It leaves a grey streak when drawn across paper. Small traces of impurity—antimony, arsenic, copper, zinc—make the lead much harder. Lead is not tough enough to be hammered into foil or drawn into wire; but it can be pressed into pipes, or rolled into thin sheets or foil. Lead filings under a pressure of about 13 tons per square inch form a solid block; and the metal seems to liquefy under a pressure of about 33 tons per square inch. The specific gravity of lead varies from 11.25 to 11.4 according as the metal is cast or rolled. Lead melts at  $327.3^{\circ}$ , and boils at  $1750^{\circ}$ . When cooled slowly, the molten metal forms a mass of octahedral crystals (cubic system). The crystalline nature of the metal is shown by the electrolysis of a lead salt. Lead is also deposited as an "arborescent" mass of crystals—called a "lead tree"—when a strip of iron or zinc is suspended in a solution of a lead salt.

Lead is fairly rapidly dissolved by warm, dilute or moderately concentrated nitric acid. Very concentrated nitric acid is almost without action. Lead is little affected by dilute hydrochloric, or dilute sulphuric acid in the cold, because a crust of insoluble lead chloride or sulphate is formed on the surface, and this protects the metal from further action. Powdered lead is quickly dissolved by boiling concentrated hydrochloric or sulphuric acid with evolution of hydrogen and sulphur dioxide respectively. Organic acids—acetic acid (vinegar)—also act as solvents for metallic lead. Hence vessels plated with tin containing lead, if used for cooking purposes, may contaminate the food with poisonous lead compounds. Water containing sulphates and carbonates in solution forms a coating on the surface of lead which prevents further action. Lead is attacked by water holding air, nitrates, ammonium salts, and carbon dioxide in solution. In the latter case, a soluble acid carbonate may be formed. All soluble lead salts are poisonous, and if the water supply of a town be pure enough to attack lead it may produce lead poisoning. To avoid risk, the water is sometimes filtered through limestone or chalk since carbonates in the water do not corrode the pipes very much. The water then takes up enough carbonates to form a film on the interior of the lead pipes which protects the lead from further action. The addition of soluble silicates, which bring about the formation of insoluble lead silicate, is also effective.

### § 18 Uses of Lead

Lead is largely used in the arts on account of the ease with which it can be worked, cut, bent, soldered, and on account of its power of resisting attack by water and many acids. It is used in the manufacture of pipes for conveying water; for the manufacture of sheaths for electric wires, sheets for sinks, cisterns, and roofs, lead chambers for

sulphuric acid works, evaporation pans in chemical works, etc. The addition of a trace (0.05 to 0.08 per cent) of tellurium renders lead much more resistant to corrosion by sulphuric acid and also improves the mechanical properties of the metal. It is used in making bullets, shot, accumulator plates, etc. Type metal, solder, pewter, and fusible alloys contain much lead. Lead is also used for the production of leaded steels in which the presence of a small quantity of lead has been found to bring about marked improvement in the machining properties.

### § 19 Atomic Weight of Lead

The atomic weight of lead has been the subject of very many investigations on account of the differing values to be expected for it according to its origin. Thus lead is the end product of radioactive change (see Chapter 12), and its atomic weight, according to modern theory, would be expected to approach 206 or 208 according as it is derived from the uranium or thorium series respectively.

The atomic weight of lead is seen to be in the neighbourhood of 207 from a consideration of its specific heat (0.0309) and the vapour density of its volatile compounds. The exact value to be used has been deduced from the conversion of highly purified lead chloride into silver chloride. For common lead (i.e., from non-radioactive sources) the value 207.21 is that adopted by the International Committee. Values for the atomic weight of radiogenic lead have been obtained as low as 205.93 and as high as 207.92, according to their source, by workers such as Richards, Honigschmid and Baxter.

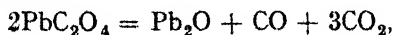
### § 20 Hydride and Oxides of Lead

An indication of the possible existence of a very unstable hydride of lead (presumably  $\text{PbH}_4$ ) was obtained by Paneth (1920) using a technique similar to that by means of which he had previously shown the existence of bismuth hydride (page 849). A magnesium-lead alloy was irradiated so as to produce thorium B (isotopic with lead) and then dissolved in hydrochloric acid. The gas (mainly hydrogen) when passed through a red-hot tube gave a radioactive deposit having the same half-life period as thorium B, thus showing that the hydrogen must have contained the hydride of this isotope of lead.

Five oxides of lead have been described, viz.:

- Lead suboxide,  $\text{Pb}_2\text{O}$ ;
- Lead monoxide, litharge, massicot,  $\text{PbO}$ ;
- Triplumbic tetroxide, red lead, minium,  $\text{Pb}_3\text{O}_4$ ;
- Lead sesquioxide,  $\text{Pb}_2\text{O}_3$ ;
- Lead dioxide,  $\text{PbO}_2$ .

**Lead suboxide**,  $\text{Pb}_2\text{O}$ , is said to be formed by heating lead oxalate out of contact with air:



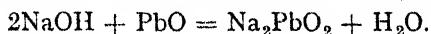
and also as a dull grey iridescent coating on the surface of lead melted at a low temperature. Its existence is still in dispute, but it now seems likely that the product of this reaction is a mixture of litharge and metallic lead. (Bircumshaw, 1939.)

### Lead Monoxide, Massicot, Litharge, PbO

There seem to be two forms of lead monoxide, known as massicot and litharge respectively. Litharge is the product when it is made at a high temperature so that the product fuses, while massicot results when the temperature is kept sufficiently low to prevent melting.

Lead monoxide can be prepared in the laboratory by heating lead nitrate, carbonate, or hydroxide; commercially it is made by heating lead to a temperature considerably above its melting point, and blowing air on to the surface, while continually removing the litharge produced.

Litharge varies in colour from pale yellow to reddish yellow, possibly owing to the existence of two forms, a yellow and a red. It fuses at  $888^{\circ}$  and is volatile at a red heat. It is slightly soluble in water, probably forming lead hydroxide (q.v.). It reacts with acids, forming solutions of lead salts, and also with alkalis forming plumbites, e.g.:



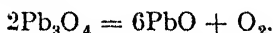
It is thus an amphoteric oxide.

Litharge is used in preparing oils and varnishes and sometimes in the manufacture of flint glass, although red lead is more often employed (page 779), as well as for the preparation of some lead salts.

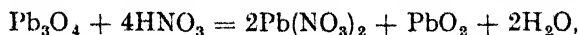
### Triplumbic Tetroxide, Red Lead, Minium, $\text{Pb}_3\text{O}_4$

Red lead is prepared from massicot—unfused lead monoxide—by heating it to a carefully regulated temperature ( $470^{\circ}$ – $480^{\circ}$ ) for several hours. The hot powder acquires a deeper and deeper tint as time goes on and appears to become violet and finally black. On cooling, the colour changes to a brilliant red.

On strong heating, red lead decomposes, forming litharge from which red lead cannot be re-formed:

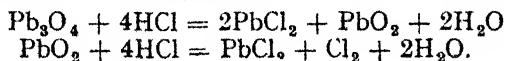


Nitric acid converts red lead into lead nitrate and lead dioxide:



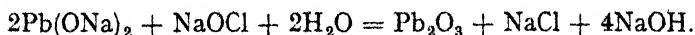
which suggests that red lead is *plumbous orthoplumbate*,  $\text{Pb}_2\text{PbO}_4$ , a view which is supported by its formation from a plumbous salt and a plumbate in solution.

With concentrated hydrochloric acid, lead chloride is formed and chlorine is liberated; possibly lead dioxide is formed intermediately:

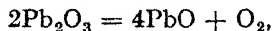


Red lead is used for a variety of purposes. It is employed in the glass industry; for making glazes for pottery; as a "cement" in making steam joints, and in the manufacture of paint, and of matches.

**Lead sesquioxide**,  $\text{Pb}_2\text{O}_3$ , is an orange-yellow powder formed by adding a solution of sodium hypochlorite to a cold solution of lead oxide in sodium hydroxide solution or by addition of dilute ammonia to a solution of red lead in acetic acid (cf. page 801):

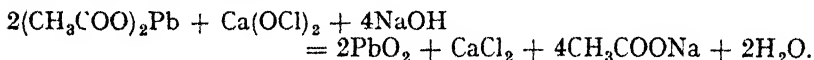


On heating, lead monoxide and oxygen are formed:



whilst with acids a lead salt and lead dioxide result. With hydrochloric acid chlorine is evolved. It is thought to be *plumbous metaplumbate*,  $\text{PbPbO}_3$ .

**Lead dioxide**,  $\text{PbO}_2$ , is best prepared by adding a solution of bleaching powder to a solution of lead acetate mixed with sodium hydroxide and boiling the mixture:



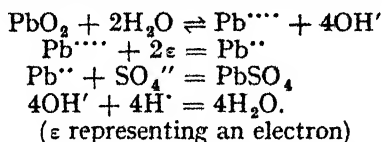
It is made commercially by heating litharge with a mixture of sodium nitrate and sodium chlorate. It is also deposited on the anode when a solution of a lead salt is electrolysed, and can be made from red lead by the action of nitric acid (*vide supra*).

Lead dioxide is a chocolate-coloured powder which, when heated, decomposes into lead monoxide and oxygen. It is a powerful oxidizing agent. Thus, when lead dioxide is gently rubbed with sulphur on a warm surface, the mass inflames; when sulphur dioxide is passed over dry lead dioxide, the two unite to form lead sulphate and the whole mass becomes red hot; and when hydrogen sulphide is allowed to impinge on a few grams of lead dioxide it bursts into flame.

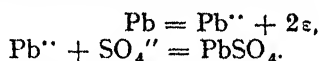
Lead dioxide is not affected by dilute acids, but it reacts with cold concentrated hydrochloric acid (probably forming lead tetrachloride,  $\text{PbCl}_4$ , page 801); with hot concentrated hydrochloric acid chlorine is evolved. It also reacts with boiling concentrated aqueous potassium hydroxide, forming *potassium metaplumbate*. This salt is often formulated as  $\text{K}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$ , by analogy with the metastannates. It seems likely that the formula  $\text{K}_2\text{Pb}(\text{OH})_6$  is more correct since it decomposes if dehydration is attempted. Lead dioxide does not give hydrogen peroxide with acids in any circumstances; hence the name "lead peroxide" is a misnomer.

Lead dioxide is an important constituent of the *lead accumulator* or storage cell. This consists essentially of an electrolytic cell having an anode of lead dioxide and a cathode of spongy lead immersed in dilute sulphuric acid (about 20 per cent). In practice, the plates consist of grids, made of lead hardened with a little antimony, into which the

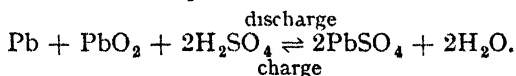
active material has been forced. This construction is adopted so as to increase the capacity of the cell and to prevent the active material from becoming detached. If the terminals of such a cell be connected through a suitable resistance a current will flow. After a time the E.M.F. of the cell, originally about two volts, drops rapidly, although it is remarkably constant until this point is reached. The cell is then said to be discharged; it can be recharged by passing a current through it in the reverse direction, from some external source. The mechanism of the changes taking place during discharge is believed to be that at the positive electrode lead dioxide is converted to lead sulphate thus:



At the negative electrode the spongy lead is similarly converted into lead sulphate with the liberation of two electrons:



These processes are reversible and during charge the reverse actions occur so that the complete cell reaction in both directions may be written as the sum of these processes at the electrodes, which is,



This mechanism is supported by the fact that the density of the electrolyte increases during charge and vice versa, corresponding with the formation, or removal, of sulphuric acid from the solution.

**Lead hydroxide**,  $\text{Pb}(\text{OH})_2$ , is formed when sodium plumbite solution undergoes slow hydrolysis on standing. The addition of a solution of an alkali hydroxide to a lead salt precipitates a white solid, of the composition  $\text{Pb}_2\text{O}(\text{OH})_2$ , which forms lead salts with acids and reacts with excess of alkali, forming solutions of **plumbites**, e.g., *potassium plumbite*,  $\text{K}_2\text{PbO}_2$ . It does not react with ammonia, and when heated to  $145^\circ$  changes to the oxide.

## § 21 Lead Salts

Lead forms compounds in which the element is either bivalent or quadrivalent; but few, if any, of the quadrivalent compounds are true salts. For example, lead tetrachloride,  $\text{PbCl}_4$  (page 801), behaves as the acid chloride of plumbic acid.

### Lead Carbonates, White Lead

Normal lead carbonate,  $\text{PbCO}_3$ , occurs native as *cerussite*, it is obtained as a white precipitate when an alkaline bicarbonate is added

to a solution of a soluble lead salt, such as the nitrate. Solutions of normal carbonates give a precipitate of a *basic lead carbonate*. Several basic carbonates of lead are known; the most important is **white lead**. This has been used as a pigment for centuries and its manufacture is an important technical operation. Several processes have been suggested, but the old so-called "Dutch" process is said to furnish the best product from the point of view of covering power when used as a pigment or in the manufacture of paints.

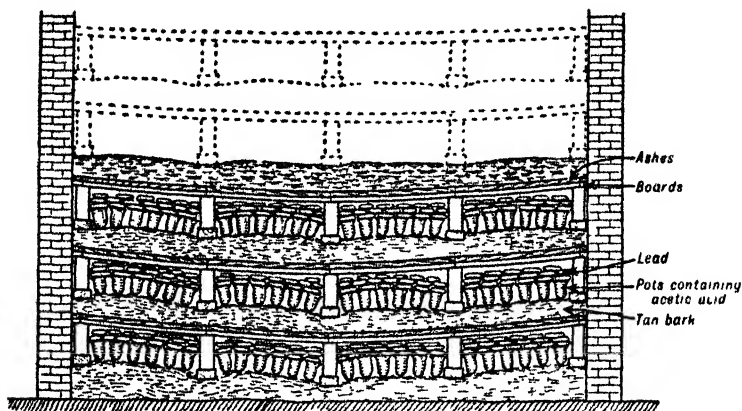


FIG. 34 5 —White Lead Stack

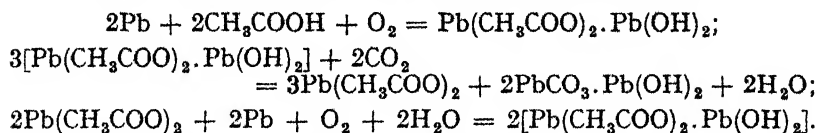
The "Dutch" process is illustrated by Fig. 34.5. There is a brick-work chamber in which is built up a stack. At the bottom is placed a layer of ashes, and then one of spent tan bark which may be up to three feet thick. On this is placed a row of pots, partly filled with dilute acetic acid. On top of these are laid perforated sheets of lead, forming a layer about five inches deep, above which is a row of boards which serve as the foundation for another tier of bark, pots and lead. The temperature of the whole stack, which should be about  $60^{\circ}$  for the best results, is carefully regulated by ventilation and the whole is left to stand for about three months. At the end of this time the stack is unloaded and the white lead crushed in a mill, any unchanged lumps of lead are removed and the residue of white lead is ground up with water.

The chemical composition is fairly constant and approximates to that required by the formula  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$  and it is probable that this is the principal constituent of white lead.

The actions taking place in the stack are thought to be as follows. The tan-bark ferments, which causes some carbon dioxide to be evolved, while heat is liberated. The heat volatilizes some of the acetic acid which reacts with the lead, forming basic lead acetate.



This is decomposed by the carbon dioxide, forming a mixture of normal lead acetate and basic lead carbonate. The acetate in presence of air and moisture reacts with more lead, forming more basic acetate, and so the process goes on. These reactions may be represented:



Many attempts have been made to speed up this process, but the quality of the products is usually inferior. A chamber process, in which the lead straps are slung over sticks resting on arches, the carbon dioxide is generated by burning weighed quantities of coke outside the chamber and water and acetic acid are evaporated in copper pots and introduced with the carbon dioxide through pipes in the floor, is in operation and is the only serious rival to the old method. The time required here is from forty to sixty days. White lead paint is the most satisfactory white pigment from the point of view of covering power, but suffers from the disadvantages that it is discoloured by hydrogen sulphide (always liable to occur in the air of towns) through the formation of black lead sulphide; and like all lead compounds, it is poisonous. Consequently other materials such as zinc oxide, lithopone (page 720), etc., are sometimes preferred.

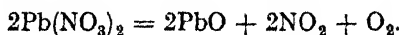
### Lead Chloride, $\text{PbCl}_2$

This salt separates as a white curdy precipitate when hydrochloric acid or a soluble chloride is added to a solution of a lead salt. It is also made by dissolving lead oxide or carbonate in hot hydrochloric acid. On cooling, the solution deposits crystals of lead chloride,  $\text{PbCl}_2$ , which melt at  $501^\circ$ . The salt is generally said to be fairly soluble in hot water, and sparingly soluble in cold water: 100 grams of water at  $0^\circ$  dissolve 0.67 gram of  $\text{PbCl}_2$ ; at  $50^\circ$  1.70 grams; and at  $100^\circ$ , 3.34 grams. When lead chloride is heated in air, **lead oxychloride**,  $\text{Pb}_2\text{OCl}_2$ , or  $\text{PbCl}_2 \cdot \text{PbO}$ , is formed. By adding hot lime-water to a boiling solution of lead chloride,  $\text{PbCl}_2 \cdot \text{PbO} \cdot \text{H}_2\text{O}$ , or  $\text{Pb}(\text{OH})\text{Cl}$ , separates. This compound is used as a white pigment under the commercial name "Pattison's white lead," and the pigment "Cassel's yellow" is a mixture containing one or more oxychlorides of lead, approximately  $7\text{PbO} + \text{PbCl}_2$ , made by heating lead oxide with ammonium chloride.

**Lead iodide**,  $\text{PbI}_2$ , forms glittering golden-yellow crystals which, like the chloride, are almost insoluble in cold water, but which are moderately soluble in hot water. (100 grams of water dissolve 0.044 gm. of lead iodide at  $0^\circ$  and 0.436 gm. at  $100^\circ$ .) It is interesting to note that the solution is colourless.

**Lead Nitrate,  $\text{Pb}(\text{NO}_3)_2$** 

Lead nitrate is formed by acting upon the metal, oxide, or carbonate with nitric acid. The salt is deposited in regular octahedral crystals which contain no water of crystallization. On heating, lead nitrate decomposes into litharge, nitrogen peroxide and oxygen, a reaction which is sometimes used for the preparation of nitrogen peroxide (page 465):

**Lead Sulphide,  $\text{PbS}$** 

Lead sulphide occurs in nature as galena in well-formed cubic crystals with a lustre resembling metallic lead. Lead sulphide is formed by reducing the sulphate with carbon, by heating lead in sulphur vapour, and as a black precipitate by passing hydrogen sulphide through neutral, acid, or alkaline solutions of a lead salt. If excess of hydrochloric acid be present, an orange, yellow, or red precipitate of **lead thiocchloride**,  $\text{Pb}_2\text{SCl}_2$ , may be formed.

Boiling dilute nitric acid dissolves lead sulphide, forming lead nitrate with the separation of sulphur. Concentrated nitric acid converts it to lead sulphate on account of the oxidation of the sulphur to sulphuric acid (page 450). Unlike tin sulphides, lead sulphide is insoluble in alkaline hydroxides and sulphides. Synthetic lead sulphide melts at  $1114^\circ$ , and galena at a lower temperature; lead sulphide begins to sublime at about  $950^\circ$  *in vacuo* or in a current of an inert gas, forming small cubic crystals. Heated with free access of air, it forms lead sulphate and some litharge.

**Lead sulphate**,  $\text{PbSO}_4$ , occurs native as *anglesite*. It is formed as a white precipitate when sulphuric acid or a soluble sulphate is added to a solution of a lead salt. It is noteworthy as one of the few sulphates which are insoluble in water and it is used for the determination of lead.

**Lead chromate**,  $\text{PbCrO}_4$ , occurs naturally as *crocoisite*. It is precipitated as a bright yellow solid by adding potassium chromate solution to a solution of a lead salt. It is used as a pigment—known as *chrome yellow*, *Cologne yellow*, *lemon chrome*, etc. By boiling with alkali hydroxide solution it is converted into red *basic lead chromate*,  $\text{Pb}(\text{OH})_2 \cdot \text{PbCrO}_4$ , also used as a pigment—*chrome red*.

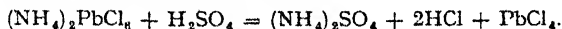
**Lead acetate**,  $(\text{CH}_3\text{COO})_2\text{Pb}$ , is important as being one of the two common salts of lead which are easily soluble in water (100 grams of water dissolve 46 grams at  $15^\circ$ ). It is made by boiling litharge with acetic acid until a solution results and allowing this solution to crystallize. It is a white crystalline salt with a sweet taste (it is very poisonous) and hence is known as *sugar of lead*. It is used in medicine, as a mordant and in the laboratory for the preparation of lead compounds.

### § 22 Quadrivalent Lead Compounds

In addition to lead dioxide, already discussed, there are a number of compounds of quadrivalent lead. Many of these are more conveniently regarded as organic compounds (as, for example, lead tetraethyl,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ , now extensively used as an "anti-knock" in motor fuels), but of the remainder, lead tetrachloride and tetra-acetate may fitly be considered here. These substances behave as covalent compounds.

#### Lead Tetrachloride, $\text{PbCl}_4$

The fact that lead dioxide will form a solution with cold concentrated hydrochloric acid has been mentioned (page 796), and is probably due to the formation of lead tetrachloride, which, in presence of excess of hydrochloric acid, is thought to form the acid  $\text{H}_2\text{PbCl}_6$ . The same deep yellow solution is obtained when chlorine is passed into a suspension of lead dichloride in concentrated hydrochloric acid. If to this solution a concentrated solution of ammonium chloride be added, yellow **ammonium chloroplumbate**,  $(\text{NH}_4)_2\text{PbCl}_6$ , separates out. This salt is stable at ordinary temperatures and can be filtered off and dried. On adding it to concentrated sulphuric acid in a good freezing mixture, lead tetrachloride is obtained as a heavy yellow liquid:



It is stable under sulphuric acid, but fumes in air at ordinary temperatures, chlorine being evolved. It is decomposed by water into lead dioxide and hydrochloric acid.

**Lead tetra-acetate**,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$ , is a white solid, obtained by dissolving red lead in a mixture of warm glacial acetic acid and acetic anhydride. The temperature must not exceed  $65^\circ$ . On cooling, the solution deposits white needles of the tetra-acetate. It is a reasonably stable compound at ordinary temperatures; latterly it has been used considerably as an oxidizing agent in organic chemistry. It is decomposed by water, forming lead dioxide.

### § 23 Detection and Determination of Lead

Lead salts in solution are detected by the formation of a white precipitate of lead chloride on addition of hydrochloric acid. This precipitate is soluble in hot water and crystallizes out on cooling in fine white needles. Lead salts also give a bright yellow precipitate of lead chromate, with potassium chromate solution.

Lead is usually determined by precipitation as the sulphate.

### § 24 Group IVA of the Periodic Table

The A sub-group of Group IV comprises the elements titanium, zirconium, hafnium and thorium. Cerium is sometimes included in this group, but, as mentioned in the previous chapter, the electronic configuration assigned to its atom by Bohr indicated that it is, properly speaking, the first member of the rare-earth elements. It shows, in fact, resemblances to both groups.

## Titanium, Ti

### History and Occurrence

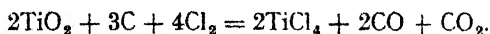
Titanium was discovered in 1791 by W. Gregor while investigating the magnetic sand (*menachanite*) found at Menachan in Cornwall, and was named by him "menachin." Three years later M. H. Klaproth found what he supposed to be a new "earth" in rutile. He called the metal derived from it titanium and showed that it was identical with Gregor's menachin. J. J. Berzelius first isolated the metal—more or less impure—in 1825.

Titanium does not occur free; but combined it is widely distributed, and in small quantities is quite common since most igneous rocks contain about 0.5 per cent. It is often thought of as a rare element; in fact, although concentrated deposits are only rarely found, it is about the tenth commonest element and more abundant than any of the common metals except aluminium and iron, and titanium and its compounds are being used increasingly. Titanium occurs in the form of its oxide  $\text{TiO}_2$ , the three polymorphic forms *rutile* (tetragonal), *brookite* (orthorhombic) and *anatase* (tetragonal) being isomorphous with stannic oxide (page 788). Titanium also occurs in the minerals *ilmenite* (titaniferous iron ore),  $\text{FeTiO}_3$ ; *sphene* or *titanite*, calcium titanium silicate,  $\text{CaTiSiO}_6$  or  $\text{CaO} \cdot \text{SiO}_2 \cdot \text{TiO}_2$ . Ilmenite and rutile are the important sources of the element.

### Extraction

At present titanium is made almost exclusively from rutile but with the prospect of increasing demand much research is going on into the possibility of using ilmenite.

In order to obtain the metal, rutile is converted into titanium tetrachloride by chlorination in presence of carbon in brick-lined shafts at  $700^\circ\text{--}1000^\circ$ :



The titanium tetrachloride is reduced by metallic magnesium (in England) with sodium in an atmosphere of argon at about  $700^\circ$ . The metal is obtained thus in the form of a sponge; vacuum distillation or leaching with 2 per cent nitric acid enables the metal to be obtained free from magnesium (or sodium) chloride but still in the form of fine granules or sponge. The production of ingots or similar forms of the metal is difficult on account of the ease with which it reacts at the high temperature required to melt it (m.p.  $1665^\circ$ ) with both the oxygen and nitrogen of the air and with refractory furnace linings. The ingots are made by melting in arc furnaces under reduced pressure in water-cooled copper crucibles.

Pure titanium is very difficult to obtain on account of the readiness with which it reacts with oxygen, nitrogen, carbon and silicon, and as its compounds with these elements have a metallic lustre and form a homogeneous mixture with the metal, their presence is often overlooked.

Titanium and titanium alloys are coming into increasing use notably in the aircraft industry. Its resistance to corrosion, particularly by sea-water, is noteworthy. This property has led to its use in marine engineering and in the chemical industry. The alloy with iron, *ferro-titanium*, is of great importance for the production of titanium steels and is used to remove oxygen and nitrogen from molten steels and as a flux in the arc-welding of steel. It is obtained by adding rutile to a molten mixture of iron and aluminium.

Titanium melts at  $1660^{\circ}$ ; when pure it is a soft light metal of specific gravity 4.5 at  $20^{\circ}$ . In chemical properties it is closely related with silicon. It burns when heated in oxygen, forming titanium dioxide; at  $800^{\circ}$  in nitrogen, it forms the nitride TiN. The metal decomposes boiling water. It is not readily attacked by acids. Hot dilute sulphuric acid yields a sulphate and hydrogen; nitric acid converts it into titanous acid,  $\text{Ti}(\text{OH})_4$ , while concentrated sulphuric acid forms the disulphate,  $\text{Ti}(\text{SO}_4)_2$ , sulphur dioxide being evolved.

Titanium gives rise to three series of compounds in which the element is bi-, ter- and quadrivalent respectively. The bivalent and tervalent derivatives are coloured, and are powerful reducing agents.

### Oxides of Titanium

Three oxides, viz.,  $\text{TiO}$ ,  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}_2$ , and the corresponding hydroxides, are known. The common oxide is the *dioxide*.

It is obtained by acting upon rutile with concentrated sulphuric acid when unstable titanous sulphate is formed along with sulphates of iron. A little water is added, which dissolves the titanium sulphate leaving most of the iron salts undissolved. The clear solution is further diluted when titanous hydroxide is precipitated and is washed and ignited leaving the dioxide.

The dioxide can also be obtained by fusing the mineral with sodium sulphide and extracting the cooled melt with water. Ferrous sulphide and titanium dioxide are left; the former is removed by dissolving it in a sulphurous acid solution. From iron titanate ores the dioxide is made by heating a mixture of the ore with carbon in a stream of chlorine. Titanium tetrachloride distils and is then hydrolysed by water to the dioxide.

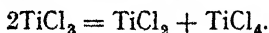
Titanium dioxide is a white powder which exists in three polymorphic forms, viz., rutile, brookite and anatase. Anatase is the stable form up to  $860^{\circ}$ , brookite is stable between  $860^{\circ}$  and  $1040^{\circ}$ , and rutile above  $1040^{\circ}$ . Titanium dioxide reacts only slowly with acids. It forms titanates when fused with alkalis, e.g., **potassium titanate**,  $\text{K}_2\text{TiO}_3$ . It is thus an amphoteric oxide. Titanium dioxide is used as a white pigment, either alone or precipitated on calcium or barium sulphate (titanox), for which it has the advantages, as compared with white lead, that it is not poisonous and does not react with hydrogen sulphide. It is also used in enamels.

**Titanium hydroxide**, titanous acid,  $\text{Ti}(\text{OH})_4$ , is precipitated from its salts

by the action of alkalis and ammonia. It resembles silicic acid in many respects. When dried it appears to form metatitanic acid,  $\text{H}_2\text{TiO}_3$ . There is some doubt about the actual existence of the acid, but well-defined metatitanates are known.

**Titanium carbide**,  $\text{TiC}$ , is harder than carborundum and is used sometimes with tungsten carbide (page 880) in cutting tools and dies.

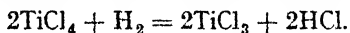
**Titanium dichloride**,  $\text{TiCl}_2$ , is made by the disproportionation of titanium trichloride by heating it *in vacuo*:



It is a very powerful reducing agent.

### **Titanium Trichloride, Titanous Chloride, $\text{TiCl}_3$**

Anhydrous titanous chloride is made by passing a mixture of the tetrachloride and hydrogen through a red-hot tube:



In solution, it is readily obtained by reduction of acidified solutions of the dioxide with zinc or tin; or by electrolytic reduction of the tetrachloride. It is a powerful reducing agent and is used in volumetric analysis for the determination of ferric iron and other oxidizing agents. The solution has a violet colour, and has to be protected from the air, which readily oxidizes it.

**Titanium tetrachloride, titanic chloride**,  $\text{TiCl}_4$ , is made by passing chlorine over a mixture of titanium dioxide and carbon or by heating ferrotitanium in a stream of chlorine. It is a volatile, colourless liquid which boils at  $136.4^\circ$ . It fumes in air, and reacts with water, giving basic chlorides or orthotitanic acid (titanium hydroxide), according to the extent of hydrolysis. In presence of excess of hydrochloric acid, the hydrolysis is almost prevented and from such solutions crystalline hydrates, e.g.,  $\text{TiCl}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{TiCl}_4 \cdot 5\text{H}_2\text{O}$ , have been obtained.

### **Zirconium, Zr**

Zirconium is widely distributed in the earth's crust in small quantities. It was discovered in 1788 in the mineral zircon by M. H. Klaproth; the metal was isolated by J. J. Berzelius in 1824.

The principal sources of zirconium are the mineral *zircon*, zirconium silicate,  $\text{ZrSiO}_4$ ; and *baddeleyite* zirconium dioxide,  $\text{ZrO}_2$ . It also occurs as various zirconates.

The metal can be produced either by electrolysis of its double potassium fluoride (obtained by fusing zircon with potassium hydrogen fluoride), or by reduction of the oxide by metallic calcium. Zirconium of a high degree of purity for radio valves is obtained by heating rods of the crude metal with iodine in an evacuated vessel, in a side chamber of which is a tungsten wire heated electrically to  $1300^\circ$ . Pure zirconium is deposited on the wire. It exists in two forms: crystalline and amorphous. It closely resembles silicon in chemical properties. It burns when heated in oxygen at a high temperature, forming the dioxide. It forms compounds in which it is bi-, ter- and quadrivalent.

It is often thought of as a rare element, but, in fact, it is estimated to be more than twice as abundant as copper and thirteen times as plentiful as lead.

Zirconium and its compounds are now finding a number of applications. Ferro-zirconium is used in the steel industry; the oxide is replacing tin oxide as an opacifier in enamel, and the metal is being used in radio valves and in "photo-flash" bulbs.

Zirconium has been used as an oxygen scavenger in the manufacture of special steels and in the construction of some wireless valves, and the dioxide has been employed as a refractory material for crucibles, etc. The oxide, silicate, carbonate and phosphate have been used in paints, and a basic acetate has found application for weighting silk, and as a mordant.

**Zirconium dioxide, Zirconia,  $ZrO_2$ ,** is a very hard, infusible white substance which is very stable and scarcely attacked by acids with the exception of hydrofluoric acid.

#### **Hafnium, Hf**

Indications of the possible existence of a new element resembling the rare earths were observed by Urbain in 1911 and by Dauvilier in 1922, but its discovery and characterization are due to Coster and Hevesy (1923). They examined a number of zirconium minerals and showed that some of them contained up to 30 per cent of the oxide of a new element; while all contained traces. The new element was named hafnium, and by examination of its X-ray spectra was shown to have an atomic number 72, and thus to fit into the vacant place in the fifth period of the Periodic Table between *lutecium* and *tantalum* indicated by the work of Bohr and Moseley.

The atomic volume of hafnium is almost exactly the same as that of zirconium. This is an example of the effect of the lanthanide contraction (page 153) and results in these elements exhibiting remarkably similar properties. One result of this is that hafnium can only be separated from zirconium by very tedious processes such as the fractional crystallization of the complex ammonium fluorides  $(NH_4)_2ZrF_6$  and  $(NH_4)_2HfF_6$ .

The metal has been obtained by heating potassium hafnium fluoride with sodium and by heating a tungsten filament in the vapour of hafnium iodide. (Cf. titanium and zirconium, *supra*.)

### **§ 25 Thorium, Th**

#### **History**

In 1818 J. J. Berzelius believed that he had discovered a new earth in a mineral from Fahlun (Sweden) and gave it the name "thoria" after the Scandinavian god Thor. In 1828 Esmark discovered a mineral from Brevig (Norway) from which Berzelius isolated an earth similar to thoria; and the mineral was subsequently called thorite. In 1898, Madame Curie and Schmidt independently observed that thorium has feeble radioactive properties. This fact may be demonstrated by flattening an incandescent gas-mantle on to the emulsion side of a photographic plate and leaving the two in contact and in complete darkness for a week. On development an image of the mantle will be obtained.

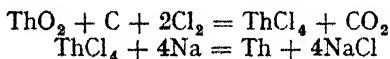
#### **Occurrence**

The principal thorium minerals are *thorite* (or *thorianite*), *gadolinite* and *orangeite*, which are silicates of very complex composition; and *monazite*, which although essentially a cerium lanthanum phosphate always contains thorium. Monazite sand is the principal commercial source of thorium compounds.

### Extraction

The principal form in which thorium is obtained is as the oxide  $\text{ThO}_2$ . It is prepared from monazite which is dissolved in concentrated sulphuric acid; the solution is then diluted and alkali slowly added. Thorium phosphate is thus precipitated before any of the other substances present and is converted into the dioxide by heating it with sodium carbonate. It is interesting to note that helium is evolved to the extent of 1 c.c. per gram (at N.T.P.) when the monazite is heated to  $1000^\circ$ , and this is now being used as a source of helium as large quantities of monazite are dealt with by the gas-mantle industry.

Thorium metal may be prepared by reduction of the chloride (obtained by the action of chlorine on a mixture of the dioxide and carbon by sodium):



or of the oxide by calcium, or by the electrolysis of potassium pentafluorothorate ( $\text{KThF}_6$ ) dissolved in a molten mixture of sodium and potassium chlorides. The pure metal is obtained by deposition on a tungsten filament heated in the vapour of thorium iodide. The metal is soft, malleable and ductile and burns in air. It melts at  $1840^\circ$ . There are, at present, no technical uses for thorium metal.

**Thorium dioxide, Thoria,  $\text{ThO}_2$ ,** is so far the only known oxide of thorium. It is made from monazite as described above, in large quantities for use in the manufacture of gas-mantles. It is a white powder, and is comparatively inert towards reagents. It dissolves in sodium carbonate solution on account of the formation of a double carbonate; it is entirely basic in its properties.

**Incandescent gas-mantles** consist essentially of a mixture of 99 per cent of thorium dioxide (thoria) with 1 per cent of cerium dioxide (ceria). They are made by weaving a mantle "hose" in ramie fibre or artificial silk and soaking this hose in a solution of thorium and cerium nitrates in the appropriate proportions. The thorium nitrate used contains a few per cent of the sulphate since this is found to result in the oxide, when formed, being more porous and bulky. Addition of beryllium nitrate has also been recommended to improve the strength of the mantle. The mantle is then dried, the "fibre" burnt away in a high-temperature flame and the skeleton of mixed oxides remaining is dipped in collodion to make it strong enough for packing, etc., until wanted for use. It is a curious fact that thoria only gives a poor light unless mixed with 1 per cent of ceria.

## § 26 The Relationships of Group IV Elements

The elements of Group IV occur in the centre of the Periodic Table and so it is to be expected that the marked differences between the A and B sub-groups in other parts of the table would be less pronounced.



This is, in fact, the case, the differences here being comparatively slight. It is also to be expected that Group IV elements will be distinctly amphoteric, as is found in practice.

The elements of the Group are divided into subgroups as indicated in Fig. 34.6.

With the exception of carbon and silicon which are mainly acidic, the elements of Group IV are metallic in nature, and, except lead and tin, have high melting points which, with the specific gravities, show the normal gradation of properties with rising atomic number. This is indicated by Tables LII and LIII.

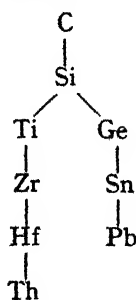


FIG 34 6

TABLE LII

Element	Melting point	Specific gravity
Titanium . .	1660°	4.5
Zirconium . .	1860°	6.4
Hafnium . .	1700°	11.4
Thorium . .	1840°	11.5

TABLE LIII

Element	Melting point	Specific gravity
Carbon . .	3500°	2.2-3.5
Silicon . .	1440°	2.4
Germanium . .	958°	5.4
Tin . .	231.9°	7.31
Lead . .	327.3°	11.34

None of these elements is more than superficially oxidized at ordinary temperatures, while all, when heated strongly, readily oxidize, forming the dioxide (except lead which forms the monoxide or red lead according to the conditions). These dioxides are acidic in the case of the lighter elements, basic character becoming more marked with increasing atomic weight.

All the elements of the group form quadrivalent compounds, and, except in the case of lead, these are the principal compounds. In all cases divalent compounds are also known, and in some (e.g., lead and titanium) trivalency is also found. One of the most marked common characteristics of the whole group is the formation of characteristic complex halogen salts of the type  $M_2M^{IV}X_6$ .

The marked differences observable in most groups between the first and later members is nowhere more noticeable than in Group IV where carbon, with its seemingly limitless ability to link itself into chains and rings and its essential relation to all forms of life, stands in a class entirely by itself. Silicon resembles carbon in many ways, but its power of forming chains, etc., is feeble by comparison.

The elements of the A sub-group show some resemblance to the rare-earth elements, but are less basic. Titanium shows marked resemblances also to silicon, thus many titanates and silicates are isomorphous, but it is much more basic in character, and this increase in basic character becomes greater with increasing atomic weight. This is shown by the decreasing hydrolysis of the quadrivalent salts on passing from titanium to zirconium, hafnium and thorium.

None of the A sub-group elements forms a definite hydroxide  $M(OH_4)$ . Attempts to precipitate them yield hydrated oxides which lose water continuously; and all readily form colloidal solutions.

In the B sub-group, germanium, tin and lead form a well-defined family, and there is a satisfactory gradation of properties from carbon through germanium to lead. But carbon and lead show no resemblance whatever comparable to that between lithium and caesium. In this respect the group more resembles Group III. The principal properties common to carbon, silicon and the B sub-group elements are: quadri-valency; formation of a hydride  $XH_4$  (very unstable in the cases of tin and lead) and oxide  $XO_2$  having acidic properties, and a liquid tetrachloride. The metallic character increases progressively with increasing atomic weight and the tendency to form bivalent compounds increases similarly.

TABLE LIV

Element	Electrons in orbits																	
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	7s
Titanium .	2	2	6	2	6	2	2											
Zirconium .	2	2	6	2	6	10	2	6	2		2							
Hafnium .	2	2	6	2	6	10	2	6	10	14	2	6	2		2			
Thorium .	2	2	6	2	6	10	2	6	10	14	2	6	10	1	2	6	1	2

TABLE LV

Element	Electrons in orbits														
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p
Carbon . . . . .	2	2	2												
Silicon . . . . .	2	2	6	2	2										
Germanium . . . . .	2	2	6	2	6	10	2	2							
Tin . . . . .	2	2	6	2	6	10	2	6	10		2	2			
Lead . . . . .	2	2	6	2	6	10	2	6	10	14	2	6	10	2	2

The probable electronic configurations of the atoms of the Group IV elements are shown in Tables LIV and LV. The close resemblance in structure in each sub-group is clear.

Carbon and silicon having four electrons in their outermost shells would not be expected to exhibit electrovalency since the loss (or gain) of the four electrons necessary to produce the Inert Gas Structure

would give rise to ions with such large charges that the energy required to bring this about would be excessive. In the case of tin and lead two of the four outermost electrons exhibit the tendency, referred to on page 732 in regard to mercury, to behave like the electrons of helium and become inert so that these elements form divalent compounds. In the case of lead, and perhaps to a lesser extent in tin, divalent ions are thus formed as well as di-covalent compounds.

Titanium, zirconium, hafnium and thorium are transition elements; the loss of the outermost electrons leaves incomplete cores as can be seen from Table LIV. The penultimate shell then contains only ten (in thorium possibly only nine) electrons. Variable valency is thus very noticeable in these elements.

Carbon, like all the elements of the first short period, cannot expand its valency group beyond eight, whereas silicon and the later elements of the Group can do so. This accounts in large measure for the differences observable between the chemistry of carbon and silicon. Compounds of silicon with four other monovalent atoms can react with other compounds with the formation of co-ionic links and expansion of the valency group of electrons to twelve. Thus, for example, silicon tetrafluoride will combine with ammonia to form  $\text{SiF}_4 \cdot 2\text{NH}_3$ , a reaction which has no parallel among carbon compounds. The ready hydrolysis of silicon tetrachloride (carbon tetrachloride is not affected by cold water) and the formation of sodium silicate by the action of sodium hydroxide on silicon tetrahydride can also be explained in this way.

## CHAPTER 35

# PHOSPHORUS AND THE REMAINING ELEMENTS OF GROUP V

### § 1 Group V of the Periodic Table

GROUP V contains the elements nitrogen and phosphorus, with vanadium, niobium, tantalum and protoactinium in the A sub-group; and arsenic, antimony and bismuth in the B sub-group.

The two light elements, nitrogen and phosphorus, are much more closely related to those of the B than of the A sub-group, and there is a well-graded variation in properties in the series nitrogen, phosphorus, arsenic, antimony and bismuth, although, as in Group IV, there is little, if any, resemblance between the first and last elements.

### § 2 Phosphorus, P. History and Occurrence

#### History

The following is probably the correct version of the discovery of phosphorus (a matter which has given rise to much confusion and doubt). Phosphorus was discovered in 1674 or 1675 by Brand of Hamburg, by a process involving the distillation of evaporated urine. He obtained the solid, though only in small quantity. At the end of 1675 or early 1676 his secret was sold to D. Krafft for £37; and he also informed J. Kunckel that it was obtained from urine. Kunckel obtained solid phosphorus from urine in 1676 after a few weeks of experimenting. Solid phosphorus was shown to Boyle and others in 1677 by Krafft, who told them that it was obtained from "part of the human body." Boyle succeeded in obtaining solid phosphorus in 1681 and was the first to publish an account of the method of making it.

The name phosphorus is derived from the Greek— $\phi\omega\varsigma$  (*phos*), light; and  $\phi\acute{\epsilon}\rho\omega$  (*phero*), I carry. It was applied to various substances, such as commercial barium and calcium sulphides, which glow in the dark, as well as to phosphorus proper; but in due course it became restricted to the element.

In 1769 G. Gahn showed that calcium phosphate occurs in bones, and C. W. Scheele obtained phosphorus from bone ash in 1771. The elementary nature of phosphorus was first recognized by A. L. Lavoisier in 1777.

#### Occurrence

Phosphorus, of course, does not occur free in nature, because it is so very readily oxidized in contact with air. It is, however, rather

widely distributed in combination with oxygen—as earthy phosphates—in such minerals as *sombrerite*, *phosphorite*, *coprolites*, and “phosphate rock” (of South Carolina, Florida, and Tennessee), all of which are more or less impure calcium phosphates,  $\text{Ca}_3(\text{PO}_4)_2$ . It also occurs in *chlor-apatite*— $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCl}_2$ ; *fluor-apatite*— $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ; *vivianite*— $\text{Fe}_3(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ; *wavellite*— $4\text{AlPO}_4 \cdot 2\text{Al}(\text{OH})_2 \cdot 9\text{H}_2\text{O}$ . Some native phosphates are valued for the rare earths associated with them, e.g., *monazite*, and some phosphates are present in certain gems, e.g., *turquoise*, *lazulite*, etc.

### The Phosphorus Cycle in Nature

Small quantities of phosphates are found in granitic rocks. By the weathering and decay of these rocks, the combined phosphorus ultimately finds its way into the soil, spring water, and the sea. All fertile soils contain phosphorus. A ton of average fertile soil contains an average of about a pound of phosphorus—phosphorus is needed to build up certain parts of the essential tissue of growing vegetation. Plants require phosphates from their earliest life, and seeds contain a plentiful supply for the germination of the embryo.

Animals feeding upon plants or upon herbivorous animals concentrate the phosphorus in their bones and tissue. The bones of an adult man furnish about  $4\frac{1}{2}$  lb. of normal calcium phosphate. A normal adult excretes the equivalent of 3–4 grams of phosphoric acid daily. This is derived from vegetable foods, and partly from the waste of muscular and nervous tissue which involves a decomposition of the phosphorus compounds. The products of decomposition are carried by the blood to the kidneys, and there excreted with the urine—chiefly as sodium ammonium phosphate.

The phosphorus discharged by animals finds its way back to the soil, or rather into the sewage and finally into the sea. The amount returned from the sea as edible fish is insignificant in comparison with that which was formerly drained into the sea as sewage from large towns.

Processes for checking the loss of phosphorus in sewage have attracted much attention, for the growing of repeated crops impoverishes the phosphate content of the soil, and this is made up by the application of phosphatic fertilizers, usually in the form of a phosphatic mineral, e.g., phosphate rock. When supplies of this material begin to run short, a serious situation will arise unless means for the recovery of the phosphorus at present lost in sewage or buried out of reach in cemeteries can be devised.

### § 3 Manufacture of Phosphorus

Phosphorus is made from calcium phosphate. Formerly bones were the principal source of this substance, but much of the phosphorus and phosphorus compounds of commerce are now derived from mineral phosphate deposits.

The bones are digested with solvents such as benzene, ether, etc., to remove fat, after which the "degreated bones" are digested with water under pressure to remove gelatine. The "degelatinized bones" remaining are heated in air when bone ash, which is mainly calcium phosphate, remains.

Two processes have been used for the manufacture of phosphorus, viz., the retort process, now obsolete, and the electrical process which is the one now used.

### The Electrical Process

In this process, which is *electrothermal* and not electrolytic, a mixture of calcium phosphate, sand and coke is fed into an electric furnace illustrated diagrammatically in Fig. 35.1. At the high temperature

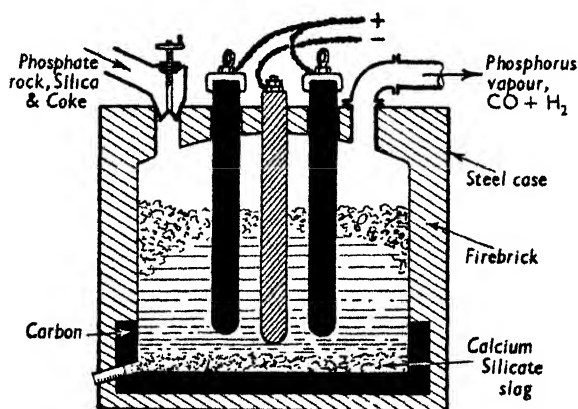
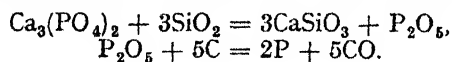


FIG. 35.1.—Manufacture of Phosphorus

of the electric furnace, the silica, on account of its involatility, displaces the phosphoric acid of the phosphate, although the latter is the stronger acid, thus forming phosphoric oxide which is reduced by the carbon to phosphorus. The phosphorus escapes as a vapour and is condensed:



### Purification

The methods employed for the purification of the crude phosphorus obtained as above are trade secrets. It is said to be purified by distillation from iron retorts, or by warming with a mixture of sulphuric acid and potassium dichromate so as to oxidize some of the impurities; other impurities rise to the surface as a scum, and leave a layer of clear and colourless phosphorus at the bottom of the tank. The molten phosphorus is then allowed to flow into a tube of half-inch bore

of such a length that the phosphorus has time to cool before it reaches the end of the tube. The phosphorus is drawn from the tube under water, and cut into sticks.

#### § 4 Properties of Phosphorus

##### Allotropy

Two well-defined allotropic modifications of phosphorus are familiar, viz., yellow (or white) phosphorus and red phosphorus. Many other alleged allotropic forms have been described (e.g., scarlet, violet and black), but it is uncertain how far these are genuine allotropes. It is now usual to consider that there are three distinct forms, yellow, red and black; the others being varieties of these. White (or yellow) phosphorus apparently consists of molecules of  $P_4$  with the phosphorus atoms arranged tetrahedrally; black phosphorus is a "giant molecule" (i.e., a three-dimensional network of interlinked phosphorus atoms) and amorphous (red) phosphorus consists of a random arrangement derived from the rupture of some of the bonds in the tetrahedral  $P_4$  molecules of yellow phosphorus.

When phosphorus vapour condenses, the yellow form results. This is metastable at all temperatures up to the melting point of red phosphorus ( $589.5^\circ$  at 43 atmospheres). The red form is the stable form, but conversion of the yellow into the red is extremely slow at ordinary temperatures. Phosphorus is therefore said to be *monotropic*; an element, like sulphur, for which there is a transition point between two forms is said to be *enantiotropic* (cf. page 476).

When yellow phosphorus is exposed to air and light; or when phosphorus is heated to about  $250^\circ$  in an inert gas or *in vacuo*; or when phosphorus is exposed to an electric discharge—silent or spark—it soon passes into a chocolate-red coloured allotropic modification which sometimes has an iron-grey metallic lustre. This is the variety called red phosphorus.

The change proceeds with almost explosive violence when the phosphorus is heated under pressure to about  $350^\circ$ ; at  $300^\circ$  the change is moderately fast. The speed of the transformation can be accelerated by the addition of a trace of iodine. In the presence of this catalytic agent, the change is fairly fast at  $200^\circ$ .

Red phosphorus is made commercially by heating yellow phosphorus in an iron pot, having a cover through which passes a long narrow, upright iron tube to prevent the development of pressure. The pot is heated to  $240^\circ$ , the temperature being carefully controlled. A little of the phosphorus burns, removing the oxygen from the air initially present; after which very little if any enters by the long tube. When the conversion to the red form appears to be complete, the product is ground with water and boiled with sodium hydroxide solution to remove any unchanged yellow phosphorus. The red phosphorus is then washed with water and dried; or, alternatively, preserved under water.

P. W. Bridgman's study of the effect of high pressures on phosphorus furnished him with an hexagonal variety of yellow phosphorus which passes into the ordinary cubic form at the transition point  $-76.9^{\circ}$ ; and a variety of black phosphorus formed at  $200^{\circ}$  under pressures from 12,000 to 13,000 kilograms per sq. cm.

### Properties of Yellow Phosphorus

Yellow phosphorus, which has also been called "octahedral," "common," "colourless," "white," and "non-metallic" phosphorus, is a translucent, almost colourless solid, which soon becomes coated with a white opaque crust. If exposed to light, yellow phosphorus rapidly darkens in colour. At  $0^{\circ}$  it is hard and brittle with a crystalline fracture; at ordinary temperatures it is soft enough to be cut with a knife. It melts at  $44.1^{\circ}$  under atmospheric pressure, and at  $52.8^{\circ}$  under a pressure of 300 atmospheres. When molten phosphorus is cooled, the temperature can be reduced much below the melting point without solidification, owing to the effects of undercooling. Phosphorus boils at  $282^{\circ}$  (760 mm.), and at  $165^{\circ}$  under a pressure of 120 mm., but it vaporizes at a much lower temperature. For instance, when phosphorus is heated to  $40^{\circ}$  in the lower part of a flask in an atmosphere of carbon dioxide, crystals of phosphorus sublime on to the upper part of the flask. Yellow phosphorus also sublimates at ordinary temperatures *in vacuo* when exposed to the light. Yellow phosphorus ignites at about  $30^{\circ}$  in air, saturated with moisture; the inflammation temperature is higher the dryer the air. When phosphorus burns in air, dense white clouds of phosphorus pentoxide,  $P_2O_5$ , are formed. If, however, the phosphorus and oxygen be perfectly dried by exposure to the desiccating action of phosphorus pentoxide phosphorus may be melted and even distilled in oxygen with very little oxidation.

The inflammation temperature is so low that the heat of the body suffices to raise the temperature of the phosphorus above its kindling temperature, and hence phosphorus should always be "handled" with the forceps, never with the bare fingers unless under water. Burns produced by phosphorus are very painful, and heal very slowly. The fumes of phosphorus are poisonous. Persons constantly exposed to their action are liable to suffer from caries (rotting) of the bones of the jaw and nose—"fossy jaw." Phosphorus itself is poisonous; it is stated that a 0.1 gram dose is fatal to man.

On account of its inflammability, phosphorus is usually preserved under water in which it is almost insoluble—one part of phosphorus dissolves in 300,000 parts of water, but it readily dissolves in carbon disulphide, sulphur chloride, phosphorus trichloride, etc.; and it is also soluble in chloroform, benzene (1.513 per cent at  $0^{\circ}$ , and 10.03 per cent at  $82^{\circ}$ ), turpentine, alcohol, ether (0.43 per cent at  $0^{\circ}$ , 2.00 per cent at  $35^{\circ}$ ), almond oil (1.25 per cent at  $15^{\circ}$ ), etc. Octahedral crystals of yellow phosphorus are obtained when the solution in carbon disulphide is allowed to evaporate. If a piece of blotting paper be



soaked with a solution of phosphorus in carbon disulphide, and the solvent be allowed to evaporate, the finely divided phosphorus which remains behind ignites spontaneously in air owing to its rapid oxidation.

When yellow phosphorus is exposed to ordinary air in the dark, it emits a pale greenish light and gives off white fumes with an unpleasant garlic-like smell.

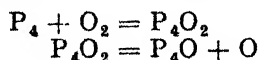
This glow of phosphorus has been the subject of much investigation, but it is still not completely understood.

Phosphorus does not glow at temperatures much below  $0^{\circ}$ , and not in inert gases—carbon dioxide, nitrogen, etc. It does not glow in pure oxygen below  $15^{\circ}$ , but it does phosphoresce if the oxygen be slightly rarefied, or diluted with an inert gas; and the glow in air is stopped if the air be compressed. The intensity of the glow is a maximum when the partial pressure of oxygen is about 300 mm. If the partial pressure of oxygen is either increased above, or diminished below, this figure the intensity of the glow is lessened; it vanishes altogether at partial pressures of oxygen greater than 600 mm. or less than 1 mm. of mercury. This lower limit is affected to some extent by the size and shape of the containing vessel being lower in a large vessel than in a small one. This suggests that a "wall-reaction" is involved.

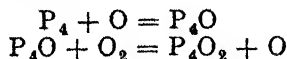
It has been established that the glow is a property of phosphorus vapour; this is deduced from the facts that the glow occurs with the vapour in the absence of solid phosphorus and that the luminous cloud can be swept away from the solid (when present) by a current of an inert gas. The glow in air is stopped if traces of gases which destroy ozone be present—e.g., hydrogen sulphide, ethylene, turpentine, etc. Hence ozone appears somehow to be connected with the phosphorescence and ozone is known to be formed when the glow occurs.

The glow is undoubtedly associated with an oxidation of the phosphorus. In moist air the product is mainly  $P_4O_6$ ; in oxygen at atmospheric pressure, it is  $P_2O_5$ ; but under reduced pressure (18–20 mm.) phosphoric pentoxide and a yellow product (thought by some to be a suboxide,  $P_4O$ ) are formed.

It has been suggested that the process involves chain reactions between phosphorus (and lower oxides of phosphorus) and oxygen atoms and that the effect of the walls is to catalyse the recombination of the oxygen atoms to form oxygen molecules. The initiation of the process may then depend upon the adventitious presence of a few oxygen atoms or (more likely) on the occurrence of reactions such as



the main chain reaction being



followed by a series of similar reactions ending with  $P_4O_6$  or  $P_4O_{10}$ .

These ideas account for the effect of the size of the vessel on the threshold partial pressure of oxygen since at low pressure in a large vessel the oxygen atoms would take longer to reach the walls. Also at higher pressures more collisions between oxygen atoms themselves (with re-formation of molecules) would occur and so the availability of oxygen atoms for the chain reaction would be reduced.

The formation of ozone can also be accounted for in this way, since it is believed to be, usually, the result of collision between oxygen atoms and oxygen molecules



Phosphorus combines directly with the halogens, forming first the trihalide and, with excess of halogen, the pentahalide (pages 829-33). It also combines with sulphur and several phosphorus sulphides are known (page 833).

Phosphorus unites directly with many metals, forming phosphides. In illustration, if very small pieces of sodium and of phosphorus be cautiously heated together, **sodium phosphide**,  $\text{Na}_3\text{P}$ , is formed. The combination occurs with a bright flash.

Phosphorus is a powerful reducing agent; the yellow variety is more active in this respect than the red. It is oxidized by nitric acid to orthophosphoric acid, and will reduce salts of copper to the metal.

Yellow phosphorus, but not red, also reacts with concentrated solutions of alkali hydroxides forming phosphine, etc. (page 819). Hence the use of sodium hydroxide for the purification of the red form.

### Properties of Red Phosphorus

Red phosphorus (sometimes called amorphous phosphorus) is the stable form of phosphorus at ordinary temperatures. It is a violet-red, apparently amorphous, powder which was shown by Pedler and Retgers in 1890 to contain rhombohedral crystals.

Red phosphorus is less chemically active than ordinary yellow phosphorus. This agrees with the fact that the passage of the yellow to the red variety is attended by an evolution of heat:

$$P_{\text{yellow}} = P_{\text{red}} + 4 \text{ Cals.};$$

and hence it is generally stated that red phosphorus contains less available energy than yellow phosphorus. Red phosphorus does not appear to volatilize appreciably below  $200^\circ$ , and only very slightly at  $280^\circ$ . Red phosphorus takes fire when heated in air to about  $260^\circ$ ; and like yellow phosphorus, previously discussed, it burns, forming phosphorus pentoxide. Red phosphorus burns if heated in an atmosphere of chlorine, whereas ordinary phosphorus takes fire spontaneously in the gas.

The difference between red and yellow phosphorus is probably as indicated on page 813. Equal weights of red and yellow phosphorus

when burnt separately in an excess of oxygen give equal weights of phosphorus pentoxide,  $P_2O_5$ .

The principal differences between red and yellow phosphorus are summarized in Table LVI.

TABLE LVI.—COMPARISON OF THE PROPERTIES OF RED AND YELLOW PHOSPHORUS

Property	Red phosphorus	Yellow phosphorus
Colour . . . . .	Reddish-violet	Almost colourless
Crystalline form . . . . .	Rhombohedral system	Cubic system
Smell, etc. . . . .	Tasteless, odourless	Garlic-like smell*
Exposed to air . . . . .	No phosphorescence, no oxidation	Phosphorescence and oxidation
Melting point . . . . .	589.5 at 43 atm.	44.1°
Physiological action . . . . .	Non-poisonous	Poisonous
Specific gravity . . . . .	2.2	1.82
Specific heat . . . . .	0.170	0.189
Action carbon disulphide . . . . .	Insoluble	Soluble
Ignition temperature . . . . .	260°	30°
Electric current . . . . .	Feeble conductor	Very feeble conductor
Hot sodium hydroxide . . . . .	Nil	Gives phosphine, etc.
Chlorine gas . . . . .	Fires if heated	Fires spontaneously

\* When undergoing oxidation

Although red phosphorus is the stable form, yellow phosphorus does not appear to pass into the red form at ordinary temperatures owing to the extremely slow velocity of the change. By the distillation of red phosphorus at 290°, yellow phosphorus is obtained, and at ordinary pressures the transition point of the stable red into the unstable yellow is masked by the vaporization of the phosphorus. However, when red phosphorus is heated under pressure in capillary tubes so as to prevent distillation, it forms a yellow liquid at 610°, and red particles begin to separate from the cooling solution at 580°. At 570° the mass turns red. Red phosphorus melts at 589.5°, under 43 atm. pressure. The vapour pressure of yellow phosphorus is greater than the red; the curves cannot be carried above 400° because the yellow phosphorus passes into the red variety so quickly at about 400°. The two vapour pressure curves are illustrated in Fig. 35.2. Both curves converge towards the

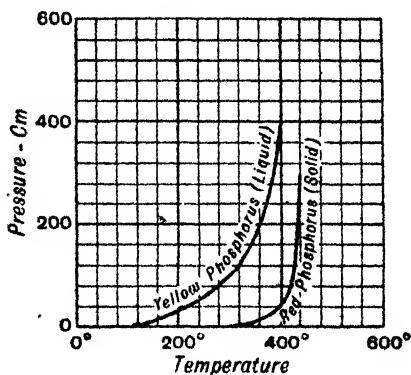


FIG. 35.2.—Vapour Pressure Curves of Phosphorus

melting point of red phosphorus at 43 atm. as is the case with allotropic modifications of other elements. It is inferred that both varieties would be in equilibrium with the vapour phase at this melting point were it not for the disturbing phenomenon just indicated.

### Other Varieties of Phosphorus

Although red phosphorus is practically insoluble in solvents such as turpentine which dissolve the yellow form, it will dissolve in phosphorus tribromide.

If the solution in phosphorus tribromide be exposed to light, or boiled for some time, what is supposed to be a mixture of red phosphorus and phosphorus tribromide separates as a scarlet-red powder—**Schenck's scarlet phosphorus**. This resembles red phosphorus in many of its properties, but is rather more chemically active, as might be expected from its extremely fine state of subdivision. This variety of red phosphorus has not been prepared free from the solvent in which it is formed.

Another variety of red phosphorus has been obtained by heating the ordinary red form with metallic lead in a sealed tube at 500° for eighteen hours.

The lead dissolves the phosphorus at the high temperature, and rejects the dissolved phosphorus on cooling in the form of rhombohedral crystals. The lead can be dissolved away by means of dilute nitric acid followed by boiling with concentrated hydrochloric acid; the residue has a specific gravity varying from 2.34 to 2.39. This dense form of red phosphorus is sometimes called Hittorf's phosphorus, or **metallic phosphorus**, or "rhombohedral" phosphorus. The term "metallic" appears to be a misnomer, for it does not conduct electricity. The specific gravity of red phosphorus varies with its method of preparation from 2.05 to the maximum 2.39 for Hittorf's phosphorus.

### § 5 Uses of Phosphorus

The most important use of elemental phosphorus is for the manufacture of matches. Yellow phosphorus was formerly employed, but on account of its poisonous properties its use has been abandoned.

The modern "strike-anywhere" match-head usually contains a phosphorus sulphide,  $P_4S_3$ , together with potassium chlorate or manganese dioxide, glue, powdered glass to increase friction, and a colouring matter such as prussian blue or chrome yellow. Safety matches have a head composed of oxidizing agents, such as potassium chlorate and red lead, together with antimony sulphide, and sometimes sulphur and charcoal; while the box has on it a composition containing glass and red phosphorus.

A certain amount of phosphorus is also used in the manufacture of phosphorus tri- and pentachlorides which are required for some

branches of chemical industry, e.g., the manufacture of chloro-sulphonic acid for saccharine manufacture, etc. Phosphorus is also employed in the manufacture of rat-poisons, fireworks, smoke-bombs, etc.; and is used in the making of phosphor-bronze.

### § 6 Atomic and Molecular Weight of Phosphorus

The atomic weight of phosphorus is seen to lie in the neighbourhood of 31 from a consideration of the molecular weights and composition of its volatile compounds, such as phosphine, phosphorus trichloride, etc. The determination of the accurate value has proved somewhat difficult on account of the nature of the materials involved. Among the methods which have been employed are the deposition of silver from silver nitrate by phosphorus; the conversion of silver phosphate into silver bromide; the synthesis of pure phosphorus tribromide from the pure elements and its conversion into silver bromide; the determination of the density of phosphine; and the conversion of phosphorus oxychloride into silver chloride. The value at present recommended by the International Committee is 30.975, and is based on the work of Honigschmid who prepared very pure phosphorus oxychloride and oxybromide, decomposed them with ammonia solution in a closed vessel and thus compared them with silver, and silver chloride and bromide respectively. Mass spectroscopic measurements and nuclear reaction data also lead to the value 30.975 (Motz, 1951).

The vapour density of phosphorus at temperatures between 500° and 700° corresponds with a molecule  $P_4$ ; but at higher temperatures dissociation occurs; probably into molecules of  $P_2$ ,  $P_4 \rightleftharpoons 2P_2$ . At very high temperatures, it is probable that still further dissociation into single atoms takes place.

### § 7 Hydrides of Phosphorus

#### Phosphine, $PH_3$

Phosphine is probably formed in small quantity by the decay of organic matter; and the faint luminosity seen over bogs or marshes and described as "will-o'-the-wisp" has been ascribed to it.

It is most conveniently prepared by the action of concentrated (30 to 40 per cent) sodium hydroxide solution on yellow phosphorus, in the apparatus indicated in Fig. 35.3. A mixture of sodium hydroxide solution and yellow phosphorus is placed in the flask fitted with delivery tube, etc., as illustrated in the diagram. A current of an inert gas—coal

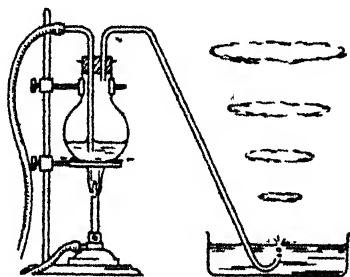
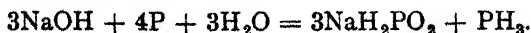


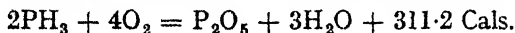
FIG. 35.3 — Preparation of Phosphine

gas, hydrogen or carbon dioxide—is first led through the apparatus to drive out the air. The mixture in the flask is then heated. The phosphorus reacts with the alkali, forming sodium hypophosphite, and gaseous phosphine,  $\text{PH}_3$ , associated with some impurities. The reaction is usually represented by the equation:

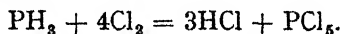


But it is almost certainly more complex than this because considerable quantities of hydrogen are formed as well as the so-called liquid hydride,  $\text{P}_2\text{H}_4$ , the presence of which causes phosphine prepared in this way to be spontaneously inflammable. As each bubble of gas rises to the surface of the water, and comes into contact with the air, it ignites with a slight explosion and burns with a brilliant flash of light, forming a vortex ring of phosphorus pentoxide. If the gas be passed through a tube immersed in a freezing mixture, it no longer inflames on contact with the air; pure phosphine is not spontaneously inflammable.

Phosphine is a colourless gas which smells like decaying fish. It liquefies about  $-89.7^\circ$ , solidifies about  $-133.7^\circ$ , and ignites when heated to about  $100^\circ$ . It burns in air, forming phosphorus pentoxide:



If a mixture of oxygen and phosphine be suddenly rarefied, an explosion occurs. The phenomenon recalls the effect of rarefaction on the luminosity of phosphorus in oxygen gas. Nitric acid or chlorine when brought in contact with the gas causes inflammation. A jet of phosphine inflames and burns, forming phosphorus pentachloride, when placed in chlorine gas:



Phosphine is slightly soluble in water: 100 volumes of water dissolve about 26 volumes of the gas at  $17^\circ$ . The aqueous solution is not alkaline like aqueous ammonia; it decomposes on exposure to light and deposits red phosphorus. The gas possesses reducing properties, e.g., when passed into solutions of copper sulphate,  $\text{CuSO}_4$ , or mercuric chloride,  $\text{HgCl}_2$ , phosphine precipitates phosphides of the metals. It combines, like ammonia, with some chlorides, for instance, aluminium chloride and stannic chloride.

### The Composition of Phosphine

J. B. Dumas determined the composition of phosphine by passing a known volume of the gas over heated copper turnings—zinc, antimony, iron and potassium have been used in place of copper. The copper forms copper phosphide. The increase in weight of the copper shows the amount of phosphorus in the volume of the gas which has reacted. The escaping hydrogen is collected and measured. Experiment shows that 34 parts of phosphine by weight give 31 parts of

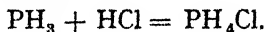
phosphorus and 3 parts of hydrogen. The empirical formula is therefore  $\text{PH}_3$ . Similarly, when phosphine is decomposed by the passage of electric sparks through the gas, one volume of phosphine gives  $1\frac{1}{2}$  volumes of hydrogen, and red phosphorus, of negligibly small volume in comparison with the volume of the gas, is deposited on the walls of the tube. Hence two volumes of phosphine furnish three volumes of hydrogen; otherwise expressed, by Avogadro's hypothesis, two molecules of phosphine give three molecules of hydrogen:

Hence the formula must be  $\text{P}_n\text{H}_3$  where  $n$  is still to be determined.

The vapour density of phosphine is 17 ( $\text{H}_2 = 1$ ), hence  $n = 1$ , and the formula is  $\text{PH}_3$ .

### Phosphonium Compounds

When dry phosphine is brought into contact with dry hydrogen chloride, bromide or iodide at high pressures, the gases unite, forming phosphonium compounds, e.g.,

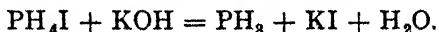


This behaviour is reminiscent of that of ammonia which forms ammonium compounds in a similar manner (page 434), and the radical,  $\text{PH}_4$ , phosphonium, is analogous to  $\text{NH}_4$ , ammonium. Phosphine is, however, a very much feebler base than ammonia.

The best-known phosphonium salt is **phosphonium iodide**,  $\text{PH}_4\text{I}$ . It is made by dissolving phosphorus and iodine in carbon disulphide in a retort, and then distilling off the carbon disulphide. The residue is then treated drop by drop with the exact quantity of water indicated by the equation (below), and the phosphonium iodide is sublimed through a wide tube into a bottle, in a stream of carbon dioxide. The reaction is represented:



Phosphonium iodide crystallizes in large quadratic prisms with a brilliant lustre. It is an unstable salt readily dissociating into hydrogen iodide and phosphine, even at as low a temperature as  $30^\circ$ . The crystals can be sublimed without melting. They fume in air, and in contact with water form hydrogen phosphide and hydrogen iodide. With potassium hydroxide, fairly pure phosphine is obtained:



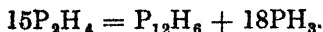
Phosphonium iodide is used as a reducing agent, and in the preparation of organic phosphines.

### Phosphorus Dihydride, Liquid Hydrogen Phosphide, $\text{P}_2\text{H}_4$

When calcium phosphide,  $\text{Ca}_3\text{P}_2$ , is treated with water, and the gas evolved is passed through a spiral tube in order to condense water, and then through a U-tube immersed in a freezing-mixture of ice and

salt, a colourless liquid is obtained which is spontaneously inflammable when exposed to air. This is the so-called liquid hydrogen phosphide, and is a colourless liquid which boils at  $57^{\circ}$  to  $58^{\circ}$ . It decomposes on standing, yielding the solid hydride (see below). Its empirical formula is  $\text{PH}_2$ ; the vapour density corresponds approximately with the molecular formula  $\text{P}_2\text{H}_4$ , which is analogous with hydrazine  $\text{N}_2\text{H}_4$ .

**Solid phosphorus hydride**,  $\text{P}_{12}\text{H}_6$ , is also formed in the reaction between calcium phosphide and water, and also when the liquid phosphide is exposed to light, or heated above its boiling point:



It is a yellow solid, which is decomposed by heat into phosphine and phosphorus. Its empirical formula is  $\text{P}_2\text{H}$ ; but the depression of the freezing point of its solution in molten phosphorus corresponds to a molecule,  $\text{P}_{12}\text{H}_6$ .

Royen and Hill (1936) have suggested that this hydride consists of phosphorus with an adsorbed layer of phosphine and that it is not a true hydride.

Several other solid hydrides have been reported, but there is some doubt about their real existence.

### § 8 Oxides of Phosphorus

Three oxides of phosphorus are definitely known, viz.:

Phosphorous oxide, phosphorus trioxide,  $\text{P}_2\text{O}_3$  or  $\text{P}_4\text{O}_6$ ;

Phosphorus tetroxide,  $\text{P}_2\text{O}_4$ ;

Phosphorus pentoxide,  $\text{P}_2\text{O}_5$  or  $\text{P}_4\text{O}_{10}$ .

A suboxide has also been reported, but is probably impure red phosphorus; a peroxide  $(\text{PO}_3)_n$ , described by Schenck and Platz (1936), awaits confirmation.

**Phosphorous oxide**, phosphorus trioxide,  $\text{P}_2\text{O}_3$  or  $\text{P}_4\text{O}_6$ , is formed, along with phosphorus pentoxide, when phosphorus is burned in a

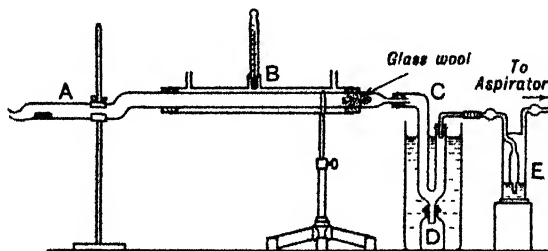


FIG. 35.4.—Preparation of Phosphorous Oxide

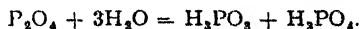
limited supply of air. Some yellow phosphorus is placed in a glass tube A, bent as shown in Fig. 35.4, and fitted into one end of a long



tube cooled by a jacket *B* containing water at 60°. The cooled tube is fitted to a U-tube *C* immersed in a freezing mixture; a plug of glass-wool is placed in the condenser tube near the U-tube. The phosphorus is ignited, and a slow stream of air is drawn through the apparatus by means of an aspirator connected to the U-tube. The phosphorus pentoxide is arrested by the glass-wool, and phosphorous oxide passes into the U-tube, where it is condensed into a white crystalline mass. The wash-bottle *E*, with concentrated sulphuric acid, protects the product from moisture. At the end of the experiment, the solid in the U-tube can be melted and run into the bottle *D*.

Phosphorous oxide, so obtained, is a mass of monoclinic prisms, which melts at 22.5° and boils at 173°. It smells like garlic and is poisonous. When exposed to the air, it is gradually oxidized to the pentoxide, and when placed in warm oxygen it bursts into flame. It also ignites spontaneously in chlorine. It is slowly attacked by cold water, forming phosphorous acid,  $\text{H}_3\text{PO}_3$ , and with hot water it forms red phosphorus, and phosphine along with phosphoric acid. The vapour density corresponds to the formula  $\text{P}_4\text{O}_6$ , while the lowering of the freezing points of its solutions in benzene and naphthalene indicates the same value. The molecule has a tetrahedral configuration with a phosphorus atom at each apex and an oxygen atom in the middle of each edge.

**Phosphorus tetroxide**,  $\text{P}_2\text{O}_4$ , is obtained by heating phosphorus trioxide in a sealed tube to 440°, when the trioxide decomposes, and the tetroxide appears as a crystalline sublimate. It is thus obtained in colourless, transparent crystals, which with water form a solution consisting of a mixture of phosphorus and phosphoric acids.



It is thus analogous to nitrogen tetroxide (page 467).

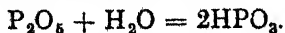
### Phosphorus Pentoxide, Phosphoric Oxide, $\text{P}_2\text{O}_5$ or $\text{P}_4\text{O}_{10}$

When phosphorus is burnt in an excess of dried air or oxygen, white clouds of phosphorus pentoxide condense as a voluminous powder. Small quantities of other oxides may be formed at the same time and it is best purified by heating it to 600°–700° in an iron tube attached to a glass tube through which oxygen is passing at a fairly rapid rate. The pentoxide is vaporized and condenses in the glass tube.

Phosphorus pentoxide is a white solid, which is said to exist in three forms: crystalline, amorphous and vitreous. The exact number and relation of the forms is still in doubt. It sublimates very slowly at 50°, but at 250° the sublimation is rapid. The vapour density at 1400° corresponds with the molecular formula  $\text{P}_4\text{O}_{10}$ ; but the simpler formula,  $\text{P}_2\text{O}_5$ , is often adopted for convenience and on account of our ignorance of the molecular formula of the *solid* oxide.

Phosphorus pentoxide is extremely hygroscopic, and it absorbs moisture from the air very quickly; hence its use for drying gases. When thrown into water, combination occurs with a hissing sound

resembling the quenching of red-hot iron, and metaphosphoric acid is formed:



When this solution is boiled with water, or when the phosphorus pentoxide is thrown into hot water, orthophosphoric acid is formed:



The affinity of phosphorus pentoxide for water is so great that, as well as being the most powerful drying agent known, it can withdraw the elements of water from many organic and inorganic compounds. Thus, it converts nitric acid into nitrogen pentoxide (page 468). The acid— $\text{P}(\text{OH})_5$ , the true ortho-acid—is not known.

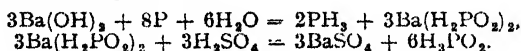
### § 9 The Acids of Phosphorus

The best-defined acids of phosphorus are:

Hypophosphorous acid,  $\text{H}_3\text{PO}_2$ ,  
 Phosphorous acid,  $\text{H}_3\text{PO}_3$ ,  
 Hypophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_6$ ,  
 Orthophosphoric acid,  $\text{H}_3\text{PO}_4$ ,  
 Pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ ,  
 Metaphosphoric acid,  $\text{HPO}_3$ .

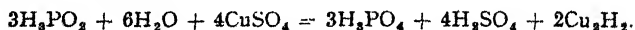
#### Hypophosphorous Acid, $\text{H}_3\text{PO}_2$

When yellow phosphorus is heated with alkalis (as in the preparation of phosphine, page 819) hypophosphites are formed. If barium hydroxide be used, free hypophosphorous acid can be obtained from the product by addition of the calculated quantity of sulphuric acid.



After filtering the precipitated barium sulphate, the solution can be concentrated by evaporation and hypophosphorous acid obtained as a colourless crystalline solid, melting at  $26.4^\circ$ .

Hypophosphorous acid is a monobasic acid (i.e., only one of the three hydrogen atoms is replaceable by a metal). The acid and its salts are very powerful reducing agents; thus, with copper sulphate, a red precipitate, believed to be copper hydride,  $\text{CuH}$ , is obtained:

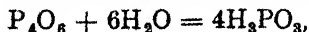


This reaction is used for the detection of hypophosphites.

Hypophosphorous acid is itself reduced by zinc and hydrochloric acid to phosphine. The constitution of the acid is discussed, along with that of other acids of phosphorus, below (page 828).

#### Phosphorous Acid, $\text{H}_3\text{PO}_3$

This acid is formed by the action of water upon phosphorous oxide:



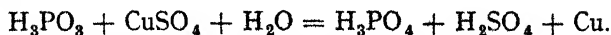
or by the action of water on phosphorus trichloride:



or by passing a stream of chlorine through water beneath which phosphorus is melted. The solution is evaporated until the temperature has reached  $180^{\circ}$ , when, on cooling, it solidifies to a crystalline solid which melts at  $73.6^{\circ}$ . When heated, phosphorous acid decomposes into phosphine and orthophosphoric acid:



It is a powerful reducing agent and reduces salts of copper, etc., to the metal, e.g.:

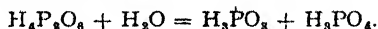


It also absorbs oxygen, forming phosphoric acid; while it is reduced by zinc and hydrochloric acid to phosphine.

Phosphorous acid is a dibasic acid. Its salts—the **phosphites**—are soluble in water, and like the acid are strong reducing agents. Those of the alkali metals have an alkaline reaction in solution. A number of salts is known, derived from various polyphosphorous acids, by removing molecules of water from one or more molecules of an ordinary phosphite. Of these, pyrophosphites, from  $\text{H}_4\text{P}_2\text{O}_5$ , and metaphosphites, from  $\text{HPO}_2$ , may be mentioned.

#### Hypophosphoric Acid, $\text{H}_4\text{P}_2\text{O}_6$

A mixture of hypophosphoric, phosphoric and phosphorous acids is formed when phosphorus is exposed to a limited supply of moist air. Hypophosphoric acid can be isolated as follows. Water made slightly acid with sulphuric or formic acid is electrolysed, using copper phosphide as anode, and copper as cathode. When the resulting solution is treated with lead acetate an insoluble precipitate of **lead hypophosphate**,  $\text{Pb}_2\text{P}_2\text{O}_6$ , is formed. This salt is filtered from the solution, and washed with hot water. The precipitate is suspended in water, and a current of hydrogen sulphide passed through the solution. Lead sulphide,  $\text{PbS}$ , is precipitated, and a solution of free hypophosphoric acid is obtained. On evaporation, the excess of hydrogen sulphide is driven from the solution, but the evaporation cannot be carried very far without decomposing the acid. Hence, the solution must be further evaporated in a desiccator *in vacuo* over sulphuric acid. In time, tabular, rhombic crystals of the hydrate  $\text{H}_4\text{P}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$  separate. The crystals melt at  $62^{\circ}$ . Further desiccation of the crystals over sulphuric acid *in vacuo* gives the anhydrous acid,  $\text{H}_4\text{P}_2\text{O}_6$ , melting at  $70^{\circ}$ . More recently the preparation of hypophosphoric acid by the oxidation of red phosphorus with sodium chlorite has been described. The acid is stable at ordinary temperatures, it is tetrabasic, and is hydrolysed by the mineral acids, forming a mixture of phosphoric and phosphorous acids:



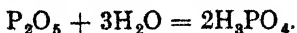
The exact molecular formula of this acid was for long in doubt, but it has now been shown that the doubled formula,  $\text{H}_4\text{P}_2\text{O}_6$ , is the correct one, on the evidence of the diamagnetism of the salts (Bell and Sugden, 1933), and of the rate of hydrolysis of the acid which indicates a unimolecular reaction (Rosenheim and Zilg, 1928).

### § 10 The Phosphoric Acids

Three well-defined phosphoric acids are known, corresponding to various degrees of condensation and dehydration of the ortho-acid.

Theoretically the true orthophosphoric acid would be  $P(OH)_6$  or  $H_6PO_6$ , but this is not known, and the first dehydration product of this hypothetical acid, i.e.,  $H_5PO_6$ , is called orthophosphoric acid. Two other acids are known derived from this acid, viz., pyrophosphoric acid,  $H_4P_2O_7$ , by loss of one molecule of water from two molecules of  $H_5PO_6$ ; and metaphosphoric acid,  $HPO_3$ , by loss of one molecule of water from one molecule of  $H_5PO_6$ .

**Orthophosphoric acid**,  $H_3PO_4$ , is formed when phosphorus pentoxide is added to water and the solution is boiled.



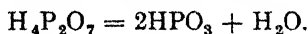
It is also formed when red phosphorus is boiled with 16 parts of nitric acid (of specific gravity between 1.20 and 1.25), and a trace of iodine, in a flask fitted with a reflux condenser. Torrents of nitrous fumes are evolved. When the action has ceased the solution is diluted with an equal volume of water, filtered and evaporated until no more acid fumes are given off, the temperature being kept below  $180^\circ$  in order to prevent decomposition of the orthophosphoric acid. It is then cooled in a vacuum desiccator over concentrated sulphuric acid; deliquescent crystals are slowly deposited.

Commercially, orthophosphoric acid is made by the action of sulphuric acid on bone ash.

Orthophosphoric acid is a colourless, syrupy liquid, which can be obtained by concentration *in vacuo* in six-sided prismatic crystals melting at  $42.3^\circ$ . It is not volatile, but dissolves readily in water with which it is miscible in all proportions. On heating, it decomposes, pyrophosphoric acid being formed at about  $250^\circ$ :



and metaphosphoric acid on further heating:



Orthophosphoric acid is a tribasic acid, and so forms three series of salts; e.g.,  $Na_3PO_4 \cdot 12H_2O$ ,  $Na_2HPO_4 \cdot 12H_2O$  and  $NaH_2PO_4 \cdot H_2O$ . The first (the normal salt) is alkaline to litmus, the second is almost neutral, and the third is acidic to litmus. Orthophosphoric acid is comparatively weak and appears to furnish ions thus at moderate dilutions:



Even at extreme dilutions, the further dissociation into  $PO_4'''$  ions is only partial. The acidic functions of the three hydrogen ions vary greatly so that, when phosphoric acid is titrated with sodium hydroxide solution, using methyl orange as indicator, the colour change takes place when  $NaH_2PO_4$  has been formed. Similarly, if phenolphthalein is used as indicator, the change takes place when  $Na_2HPO_4$  has been

formed. The acidity of the last dissociation is so slight that no indicator will indicate the formation of  $\text{Na}_3\text{PO}_4$ .

### Pyrophosphoric Acid, $\text{H}_4\text{P}_2\text{O}_7$

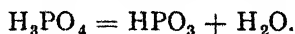
This acid is made by heating orthophosphoric acid to between  $250^\circ$  and  $260^\circ$  for some time.



It is a colourless, low melting solid which is reconverted by boiling water into the ortho-acid. It is a tetrabasic acid, as is shown by the molecular weight of its ethyl ester; but so far only two series of salts, e.g.,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$  and  $\text{Na}_4\text{P}_2\text{O}_7$ , have been obtained. The former salt is one of the products obtainable by heating sodium dihydrogen phosphate; the latter results when ordinary sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) is heated.

### Metaphosphoric Acid, $\text{HPO}_3$

This acid is formed as a viscous solid when phosphorus pentoxide is left exposed to moist air; it is also obtained by heating ammonium orthophosphate, or pyro- or orthophosphoric acid to a red heat:

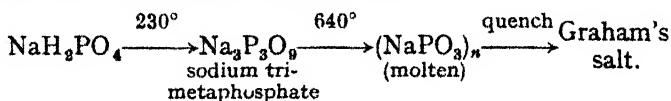


Metaphosphoric acid is a transparent vitreous solid, sometimes called *glacial phosphoric acid*. It fuses at about  $38^\circ$ – $41^\circ$ , and the commercial acid is usually cast in sticks. It is readily soluble in water, and the solution passes, slowly in the cold and rapidly on boiling, into orthophosphoric acid.

Many metaphosphates have been described; their chemistry is complex and much of the large volume of work which has been done on them is confusing and many of the published conclusions are probably inaccurate. It now seems probable that most metaphosphates are polymers; some of them seem to be polymers of relatively high molecular weight.

Sodium hexametaphosphate (so called), to which the formula  $\text{Na}_6[\text{Na}_4(\text{PO}_3)_6]$  has been assigned (although there is little experimental evidence in support of it), is made by heating sodium dihydrogen phosphate, or microcosmic salt (page 635) to redness and quenching the fused material.

This salt, also known as Graham's salt, is used for softening water under the name of *calgon* (cf. page 312). It is probable that this substance is a high polymer of uncertain molecular weight comprising a bent chain of PO groups and oxygen atoms:

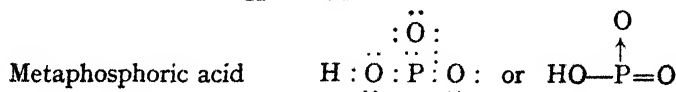
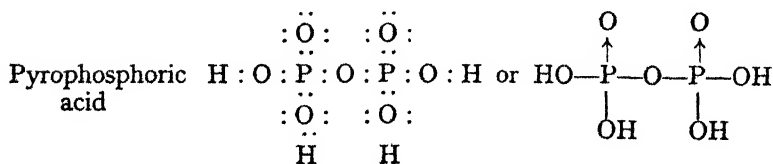
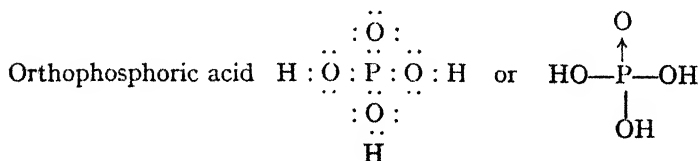
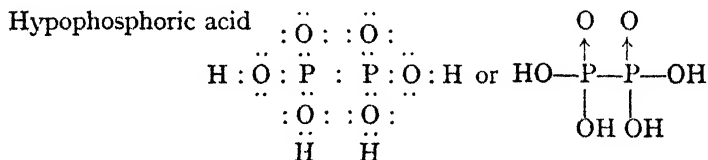
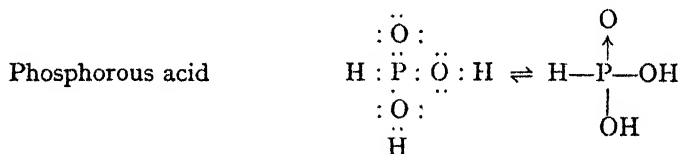
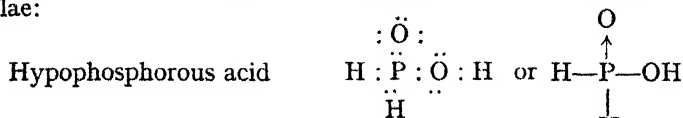


### The Structure of the Acids of Phosphorus

The structures to be assigned to the acids of phosphorus have to take into account the facts about the behaviour of these acids already mentioned; in particular that

- (i) hypophosphorous acid is monobasic;
- (ii) phosphorous acid is probably dibasic;
- (iii) phosphoric acid is tribasic; is formed from phosphorus oxychloride, and hence from phosphorus pentachloride by the action of water;
- (iv) it is probable that an hydroxyl group cannot be attached to a tervalent phosphorus atom.

These facts are now sometimes embodied in the following electronic formulae:



### § 11 Detection and Determination of Phosphates

Orthophosphates are usually detected by the formation of a yellow precipitate of ammonium phospho-molybdate on warming a nitric acid solution of the phosphate with ammonium molybdate. Metaphosphates and pyrophosphates give a similar precipitate since they are converted into orthophosphates by heating with nitric acid.

The three phosphoric acids and their salts are distinguished by the difference in their behaviour towards silver nitrate, albumen, etc., as indicated in Table LVII.

TABLE LVII.—REACTIONS OF THE PHOSPHORIC ACIDS

	Orthophosphoric acid	Pyrophosphoric acid	Metaphosphoric acid
Silver nitrate .	Canary-yellow pp.	White cryst. pp.	White gelatinous
Barium salts .	No pp. (if alkaline, white pp.)	No pp. (if alkaline, white pp.)	White precipitate
Albumen .	Nil	Nil	Coagulated
Zinc acetate .	Nil	Insoluble pp.	Nil
Aluminium salts } Chromium salts }	Soluble in acetic acid	Insoluble in acetic acid	Insoluble in acetic acid
Cobalt salts .	Blue; soluble in acetic acid	Red; insoluble in acetic acid	Red; insoluble in acetic acid
Copper salts .	Nil	Precipitate	Nil
Bismuth salt alkaline (solution) .	Nil	Nil	Precipitate

Phosphates are determined by precipitation as magnesium ammonium phosphate— $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ —by adding magnesium sulphate or chloride and ammonium chloride to the solution of the phosphate which has been made alkaline with ammonia. The magnesium ammonium phosphate which is precipitated is filtered off, washed and heated to redness. It is thus converted into magnesium pyrophosphate— $\text{Mg}_2\text{P}_2\text{O}_7$ —and is weighed as such:

Phosphates which are soluble in water or acetic acid may be determined volumetrically by titration with uranyl nitrate or acetate solution, in presence of ammonium acetate. Potassium ferrocyanide is used as external indicator:

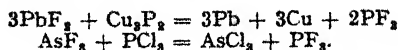


### § 12 The Halides of Phosphorus

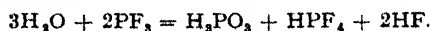
Phosphorus forms two series of compounds with the halogens, represented by the general formulae  $\text{PX}_3$  and  $\text{PX}_5$ . It is doubtful if the penta-iodide has been obtained, but otherwise all the members of both series are known. The oxyhalides  $\text{POX}_3$  are also known.

**Phosphorus Trifluoride,  $\text{PF}_3$** 

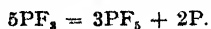
Phosphorus trifluoride is made by the action of copper phosphide on lead fluoride; or by allowing arsenic fluoride to drop slowly into phosphorus trichloride with the exclusion of moisture:



It is a colourless gas, which can be condensed to a liquid boiling at  $-95^\circ$ , and frozen to a solid, melting at  $-160^\circ$ . With water, it forms hydrofluoro-phosphoric acid and phosphorous acid:



When subjected to electric sparks, it decomposes into the pentafluoride:

**Phosphorus Pentafluoride,  $\text{PF}_5$** 

This compound is made by the action of arsenic trifluoride on phosphorus pentachloride:



It is a colourless gas which is hydrolysed by water, and which condenses to a liquid boiling at  $-75^\circ$ , and freezes to a solid, melting at  $-83^\circ$ . The vapour density of phosphorus pentafluoride is normal, viz., 63 ( $\text{H}_2 = 1$ ).

**Phosphoryl fluoride, phosphorus oxyfluoride,  $\text{POF}_3$** , is a gas obtained by sparking the trifluoride with oxygen, resembling the oxychloride (q.v.) in properties, which condenses to a colourless liquid, boiling at  $-40^\circ$  and freezing to a white solid m.p.  $-68^\circ$ .

**Phosphorus Trichloride,  $\text{PCl}_3$** 

This compound is made by the action of dry chlorine on yellow phosphorus in the apparatus indicated in Fig. 35.5.

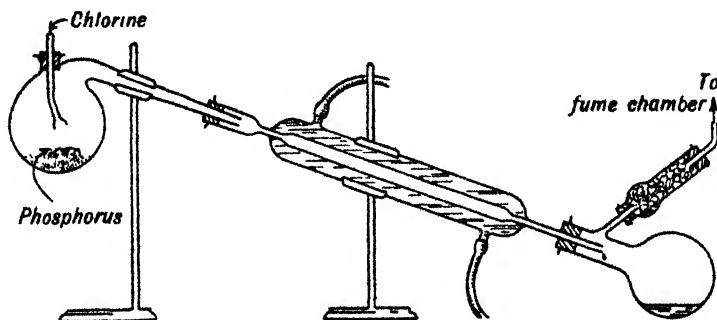


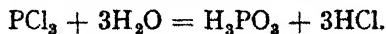
FIG. 35.5. Preparation of Phosphorus Trichloride

This consists of a retort containing a layer of sand on which rests a quantity of dry yellow phosphorus, the air having been displaced by carbon dioxide. The retort is heated gently. Chlorine, dried by sulphuric acid, is passed in by means of a movable tube. The distance of this tube is so arranged that the phosphorus does not distil (which occurs if it is too near), neither is the pentachloride formed (which happens if it is



too far off). When the action has begun, a tongue of flame projects from the chlorine tube, and the retort does not need any further heating, until at the end it is warmed gently to drive the last of the trichloride into the receiver. The product is purified by redistilling it over yellow phosphorus to convert any pentachloride present into trichloride.

Phosphorus trichloride is a mobile liquid with an unpleasant smell. It boils at  $73.5^\circ$ , fumes in air and is hydrolysed by water, forming phosphorous acid and hydrochloric acid:

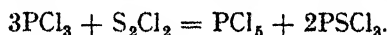


It can be frozen to a solid which melts at  $-111.8^\circ$ .

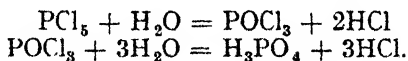
**Phosphorus pentachloride**,  $\text{PCl}_5$ , is best prepared by the action of excess of chlorine on the trichloride. It is convenient to prepare it in the vessel in which it is to be stored, as shown in Fig. 35.6.



It can also be made by the direct action of chlorine on yellow phosphorus; or by the action of sulphur chloride on phosphorus trichloride:



Phosphorus pentachloride when pure is an almost colourless solid; as obtained it is usually pale greenish-yellow. It sublimes below  $100^\circ$ , but if heated under pressure melts at  $148^\circ$ . It reacts violently with water, forming first the oxychloride, and then orthophosphoric acid:



Like phosphorus trichloride, it is a valuable reagent for transforming hydroxyl compounds into chlorides, and finds extensive use for this purpose in organic chemistry.

The vapour density of phosphorus pentachloride varies with temperature. The following values were obtained by J. B. Dumas:

Temperature . . . . .	$182^\circ$	$200^\circ$	$250^\circ$	$300^\circ$
Vapour density . . . . .	73.3	70	57.6	52.4

The theoretical value for  $\text{PCl}_5$  is 104.25 ( $\text{H}_2 = 1$ ). It is inferred, therefore, that dissociation is taking place into free chlorine and phosphorus trichloride:



This has been confirmed experimentally by the facts that starch potassium iodide papers give the characteristic blue coloration produced

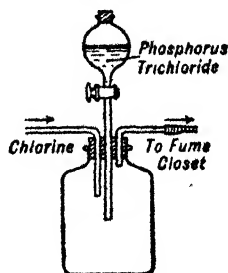


FIG. 35.6.  
Preparation of Phosphorus Pentachloride

by chlorine when immersed in the vapour of phosphorus pentachloride; and that addition of chlorine reduces the amount of dissociation as would be expected from the application of the Law of Mass Action to the equilibrium. Thus, with the notation previously employed we have:

$$\frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = K$$

Consequently, if the concentration of chlorine or of phosphorus trichloride be raised, by addition of one or other to the system in equilibrium, some combination will take place and the concentration of the pentachloride will be thereby increased. That is, its dissociation will be reduced.

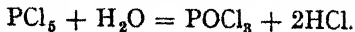
This expectation was confirmed experimentally by H. Wurtz in 1873. He found that if the pentachloride be volatilized in an atmosphere of the trichloride, the vapour density is nearly normal, 103.3 between 160° and 175°.

It has been argued that because phosphorus pentachloride splits up so readily into the trichloride and chlorine, two of the chlorine atoms in the pentachloride are differently linked to the phosphorus atom. Sugden used this argument in support of his suggestion that two of the chlorine atoms are united to the phosphorus atom by single-electron links, thus making it possible to construct a model of the molecule without increasing the number of electrons in the outermost (valency) shell of the phosphorus atom beyond eight. The inference is, however, logically invalid, for although a molecule so constructed would indeed be expected to dissociate in the way observed, it does not follow that no other cause of the observed phenomena is possible. Or otherwise expressed, the converse of the statement is not necessarily true. It might be, for instance, that the behaviour of phosphorus pentachloride is due to overcrowding of chlorine atoms round the phosphorus atom.

It may be noted that phosphorus pentafluoride gives a normal vapour density. Also, it has now been shown (Clark, Powell and Todd, 1942) as a result of X-ray examination that the solid is composed of a lattice of  $\text{PCl}_4^+$  and  $\text{PCl}_6^-$  ions.

### Phosphoryl Chloride, Phosphorus Oxychloride, $\text{POCl}_3$

This compound can be made by very carefully adding water to phosphorus pentachloride until the solid disappears:

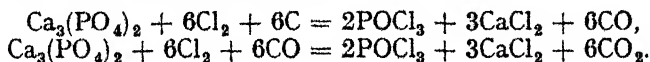


It is also made by gradual addition of powdered potassium chlorate to phosphorus trichloride at ordinary temperatures, and distillation of the mixture:



It is now manufactured from finely ground phosphate rock which

is mixed with activated coke and then treated with chlorine (sometimes mixed with carbon monoxide) at 400°.



Phosphorus oxychloride is a colourless fuming liquid which boils at 107·2° and can be solidified to a colourless crystalline mass melting at -1·25°. In aqueous solution it is slowly hydrolysed to phosphoric and hydrochloric acids.

#### Phosphorus Tribromide, $\text{PBr}_3$

Phosphorus tribromide is made by gradually adding a solution of bromine in carbon disulphide to dry red phosphorus; or to a solution of phosphorus in carbon disulphide; or better, to phosphorus covered with a layer of benzene. After the action is over, the solvent is distilled off, after which the phosphorus tribromide is distilled. It closely resembles the trichloride in properties, but is denser, and it boils at 172·9°.

**Phosphorus pentabromide,  $\text{PBr}_5$ ,** is made by the action of bromine on phosphorus tribromide. It is a yellow solid, resembling the pentachloride, but less vigorous in its reactions.

**Phosphoryl bromide,  $\text{POBr}_3$ ,** is made similarly to the chloride, and is a colourless liquid boiling at 193°.

**Phosphorus tri-iodide,  $\text{PI}_3$ ,** is made by mixing solutions in carbon disulphide of equivalent quantities of iodine and of yellow phosphorus. On distilling off the solvent, the tri-iodide remains as a reddish crystalline solid of m.p. 61°, which dissociates when heated.

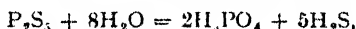
**Phosphorus di-iodide,  $\text{P}_2\text{I}_4$ ,** is obtained in orange-red crystals, which melt at 110°, when iodine and phosphorus are melted together.

**Phosphorus penta-iodide** has been reported, but its existence is doubtful.

### § 13 Sulphides of Phosphorus

Several compounds of sulphur and phosphorus have been reported of which  $\text{P}_2\text{S}_5$ ,  $\text{P}_4\text{S}_7$  and  $\text{P}_4\text{S}_8$  appear to be definite chemical compounds. They are prepared by cautiously heating appropriate proportions of sulphur and red phosphorus in an inert atmosphere (e.g., carbon dioxide).

**Phosphorus pentasulphide,  $\text{P}_2\text{S}_5$ ,** is a pale yellow crystalline mass, which melts at 276° and boils at 514°. It is hydrolysed by water.



and is used in organic chemistry for the replacement of the oxygen of hydroxy groups by sulphur.

**Phosphorus sesquisulphide,  $\text{P}_4\text{S}_3$ ,** is a grey crystalline mass, which dissolves in alkali sulphides, and is slowly attacked by water. It melts at 172·5° and boils at 407·5°. It is used in the manufacture of matches.

### § 14 Arsenic, As. History, Occurrence and Preparation

#### History

Arsenic was known to the ancients and considered by them to be a kind of sulphur. Aristotle mentions a substance, *σανδαράχη* (*sandarachē*), which appears to have been red arsenic sulphide or realgar, and was called by Theophrastus *ἀρσενικόν* (*arsenikon*), meaning "potent";

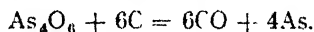
the yellow sulphide was called *auripigmentum* and *arsenicum*. The former term was afterwards contracted to *orpiment*, a term which remains with us today. The element arsenic was prepared by Albertus Magnus about 1250, and it was considered by the later alchemists to be a bastard or semi-metal.

### Occurrence

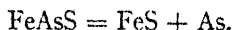
The element occurs free, and combined in a great number of minerals—oxide, *arsenolite*,  $\text{As}_4\text{O}_6$ ; sulphides, *realgar*,  $\text{As}_2\text{S}_2$ ; *orpiment*,  $\text{As}_2\text{S}_3$ ; *mispickel* or *arsenical pyrites*,  $\text{FeAsS}$ ; *cobaltite* or *cobalt glance*,  $\text{CoAsS}$ ; *arsenides*—*tin white cobalt*,  $\text{CoAs}_2$ ; *arsenical iron*,  $\text{FeAs}$ , and  $\text{Fe}_4\text{As}_3$ ; *nickel glance*,  $\text{NiAsS}$ ; *kupfernickel*,  $\text{NiAs}$ . Arsenic also occurs in most samples of pyrites and hence it finds its way into sulphuric acid when sulphur dioxide is made by roasting pyrites. Arsenic is also found in commercial zinc; and in the smoke from coal when the coal contains pyrites; hence also arsenic finds its way into the atmosphere of towns, where it can be detected, particularly in foggy weather. Arsenic is also found in some mineral waters—e.g., Levico, Roncegno, etc. A. Gautier says that traces also occur normally in the human body. The mere qualitative detection of arsenic does not therefore give much information unless the operation is more or less quantitative.

### Preparation

The element arsenic can be prepared by heating a mixture of the oxide,  $\text{As}_4\text{O}_6$ , with powdered charcoal in a clay crucible:



The crucible is provided with a conical iron cap in which the arsenic sublimes. Most of the commercial arsenic is either a natural product, or else it is made by heating *mispickel* in a clay tube fitted half its length with an inner sheet-iron tube. The arsenic sublimes into the iron tube. By withdrawing and unrolling the tube, the element arsenic is obtained:



The arsenic so obtained is not very pure. It is purified by resublimation from a mixture of the crude element and charcoal.

## § 15 Properties, Uses, etc., of Arsenic

### Properties

Like phosphorus, arsenic exhibits allotropy, and three forms are ordinarily distinguished.

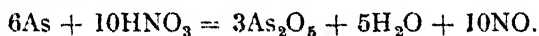
Ordinary arsenic is a steel-grey, metallic-looking substance, which forms hexagonal rhombohedral crystals with a bright lustre. This is known as **grey arsenic** or  $\gamma$ -**arsenic**. When this form is quickly heated in a current of hydrogen, black glittering hexagonal crystals are deposited nearest the hot portion of the tube, and further on a yellow

powder. The former is known as  $\beta$ -arsenic, **black arsenic** or **metallic arsenic**, and is formed by slow condensation of arsenic vapour. Its specific gravity is 4.7. At  $360^\circ$  it passes into the grey variety.

The yellow powder, known as  $\alpha$ -arsenic or **yellow arsenic**, is formed by rapid condensation of arsenic vapour. It is soluble in carbon disulphide (in which it resembles yellow phosphorus) and it is deposited from this solution in rhombohedral crystals. It is very sensitive to light, which quickly converts it into the grey variety. Its specific gravity is 2.0.

Grey arsenic is brittle, and, like the metals, it is a good conductor of heat. Its specific gravity—5.7—is higher than typical non-metals. In general physical properties grey arsenic resembles the metals, but otherwise it is classed with phosphorus among the non-metals. At atmospheric pressures it sublimes very slowly at about  $100^\circ$ , and very rapidly at a dull red heat, without melting. If heated under pressure in a sealed tube, it melts at about  $814^\circ$ , but under ordinary pressures it sublimes without melting. The vapour is lemon-yellow, and it smells like garlic. Arsenic is not altered by exposure to dry air, but in moist air a surface film of oxide is formed. At  $180^\circ$  it burns with a bluish flame, forming arsenious oxide,  $\text{As}_2\text{O}_3$ , along with a little of the pentoxide. It combines directly with chlorine at ordinary temperatures, forming arsenic trichloride,  $\text{AsCl}_3$ . It also combines directly with the other halogens and sulphur. Arsenic is insoluble in solutions of alkali hydroxides and is unattacked by those acids which are not oxidizing agents.

Dilute sulphuric acid has very little action on arsenic, but hot concentrated sulphuric acid dissolves arsenic, forming sulphur dioxide and *probably* a very unstable **arsenic sulphate**,  $\text{As}_2(\text{SO}_4)_3$ , which immediately decomposes into the oxide. Dilute nitric acid in the cold has very little action, but the hot acid oxidizes the element to arsenic acid— $\text{H}_3\text{AsO}_4$ , or  $\text{As}_2\text{O}_5$ :



Concentrated nitric acid and aqua regia also form arsenic acid.

### Uses

Arsenic is used in the manufacture of arsenic compounds, e.g., arsenic trioxide (q.v.), and in certain alloys, e.g., in the arsenical copper (0.3–0.5 per cent As), used for boiler tube plates and stays. It is used in traces for hardening lead for making shot. It is employed for the manufacture of pigments, and, by way of the trioxide, finds many uses in industry. Arsenates, particularly lead arsenate, are extensively employed as insecticides and weed-killers.

### Atomic and Molecular Weight of Arsenic

The molecular weights of volatile arsenic compounds, the position of arsenic in the Periodic Table and the application of Dulong and

Petit's Law indicate a value in the neighbourhood of 75 for the atomic weight.

Accurate determinations have been made by conversion of silver arsenate into silver bromide and silver chloride. Baxter and his collaborators synthesized very pure arsenic trichloride and tribromide and converted them into the corresponding silver halides. By this method they obtained, as the average of the results of a long series of experiments, the value 74.91. They also hydrolysed weighed quantities of the trichloride with sodium hydroxide *in vacuo* and determined the amount of iodine pentoxide exactly equivalent to this solution. The mean of these experiments was 74.911. The value at present recommended by the International Committee is 74.91.

The vapour density of arsenic at 860° is 147 ( $H_2 = 1$ ); at 1714° it is 79, and at 1736°, 77. The molecular weight at high temperatures thus corresponds to a molecule  $As_2$  and at lower temperatures to  $As_4$ .

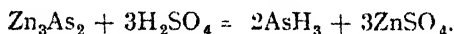
The effect of yellow arsenic on the boiling point and freezing point of carbon disulphide corresponds with a molecule  $As_4$ .

### § 16 Hydrides and Oxides of Arsenic

#### Arsenic Hydride, Arsine, $AsH_3$

Arsenic does not unite directly with hydrogen, but the hydride is produced by the action of nascent hydrogen, from zinc or magnesium and dilute hydrochloric or sulphuric acids, upon a solution containing arsenic. Arsine is also formed by the action of the nascent hydrogen from potassium hydroxide and zinc, upon solutions of arsenic compounds.

Prepared in this way, the gas is mixed with much hydrogen. It can be made almost free from hydrogen by the action of dilute sulphuric acid upon sodium arsenide or zinc arsenide:



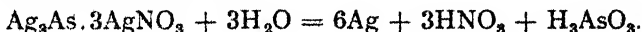
It can be obtained quite pure by drying, and then liquefying at  $-100^\circ$ .

Arsine is a very poisonous gas; one bubble is said to have produced fatal effects. It is colourless, has an unpleasant smell, and is a powerful reducing agent. It liquefies at  $-55^\circ$  and solidifies at  $-113.5^\circ$ . It is very unstable, and when heated to about  $230^\circ$ , decomposes and deposits arsenic in the form of a metallic film. It is also decomposed by electric sparks, and explodes if detonated with mercury fulminate. Arsine burns in air with a blue flame, forming arsenic trioxide; but if the flame is brought into contact with a cold surface, arsenic is deposited. The formation of arsine is used in Marsh's test for the detection of arsenic (see page 842).

With concentrated silver nitrate solution, arsine gives a yellow double compound of silver arsenide and silver nitrate:

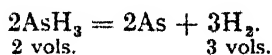


This is slowly decomposed by water with the formation of a black precipitate of metallic silver:



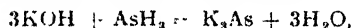
If dilute silver nitrate be used, silver is precipitated at once.

The composition of arsine can be determined by passing electric sparks through the gas, when three volumes of hydrogen are formed from two of arsine:



If the gas be passed over hot weighed copper oxide and the resulting water and copper arsenide weighed, the composition can be shown to correspond to  $\text{AsH}_3$ . The vapour density of arsine ( $\text{H}_2 = 1$ ) is 38.95, corresponding to a molecule  $\text{AsH}_3$ .

**Arsenic dihydride**  $\rightarrow \text{As}_2\text{H}_2$ , is obtained as a velvety brown powder when arsine is partially oxidized, when a jet of burning arsine impinges on porcelain; when potassium arsenide,  $\text{K}_3\text{As}$ , obtained by the reaction:



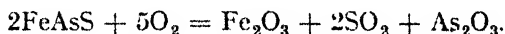
is treated with water:



when an electric discharge acts on arsine; and when water is electrolysed with an arsenic cathode

### Arsenic Trioxide, Arsenious Oxide, $\text{As}_2\text{O}_3$ or $\text{As}_4\text{O}_6$

This oxide is the most important compound of arsenic, and in commerce is often called *white arsenic*, or simply "arsenic." Small quantities occur free in nature. Arsenic trioxide is formed by oxidizing arsenic with nitric acid, and by the combustion of arsenic, which, unlike phosphorus, only oxidizes to the trioxide when burnt. It is manufactured as a by-product of the roasting of arsenical ores, such as mispickel:



This is done in a revolving, slightly sloping calcining furnace down which the ore moves, whilst furnace gases mixed with arsenic trioxide vapour pass upwards through a series of brick chambers or flues arranged so as to present an extended surface to the gases. The crude product—*arsenical soot*—is collected and refined by sublimation in a cast-iron pan covered by a bell, or from a reverberatory furnace.

Like phosphorus oxide, arsenious oxide occurs in several different forms. **Amorphous arsenic trioxide**, or vitreous arsenic, is a colourless, non-crystalline, glassy substance produced when the vapour of arsenic trioxide is *slowly* condensed at a temperature slightly below its vaporizing temperature. It melts at about  $200^\circ$ , and volatilizes at  $218^\circ$ . 100 parts of water at  $10^\circ$  dissolve 3.67 parts of vitreous arsenic oxide in six hours, the solubility diminishes on standing. Vitreous arsenic trioxide can be preserved unchanged in a sealed tube, but if it

be exposed to the air it gradually becomes opaque and forms crystals of **octahedral arsenic trioxide** belonging to the cubic system. Similar crystals are produced when the vapour of arsenic trioxide is *rapidly* condensed, and when aqueous or hydrochloric acid solutions of the trioxide are allowed to crystallize. Octahedral arsenic trioxide has less than one-third the solubility of the vitreous variety. If a hot saturated solution of arsenic trioxide in water be allowed to cool slowly in a dark room, a flash of light is produced as each crystal is formed. The specific gravity of vitreous arsenic trioxide is 3.74, and of the octahedral form, 3.63. The passage from the vitreous to the octahedral variety is attended by an evolution of heat, 5.3 cal. Octahedral arsenic trioxide vaporizes without fusion, but if heated under pressure it melts and forms the vitreous variety.

If a hot saturated solution of arsenic trioxide in potassium hydroxide be cooled, prismatic needle-like crystals of **monoclinic arsenic trioxide** separate. This variety is also formed when either of the preceding forms of arsenic trioxide is heated for a long time at 200°. Its specific

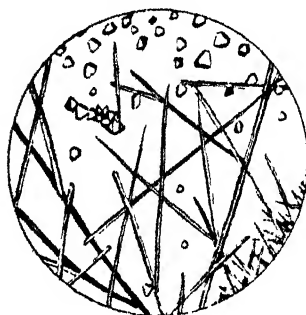


FIG. 35.7.- Dimorphism of Arsenic Trioxide

gravity is 4.15. If the lower part of a sealed tube containing arsenic trioxide be heated above 400°, the lower part will contain vitreous, the middle prismatic (monoclinic), and the upper part octahedral (cubic) arsenic trioxide. This experiment is due to H. Debray (1864). A mixture of the prismatic and octahedral crystals will be found in the zone between the octahedral and prismatic crystals. Fig. 35.7 will give some idea of the crystals in the intermediate zone as they appear magnified under a 1½-inch objective. The vitreous form is the unstable variety, and the octahedral form the stable variety at ordinary tem-

peratures. The vitreous variety can exist at ordinary temperatures because of the slow speed of transformation into the octahedral form. At 100° the speed is quite fast. At higher temperatures still the octahedral form passes into the monoclinic variety. Pressure alone (2500 kgm. per sq. cm.) at 150° will transform arsenic trioxide into the vitreous variety.

All three varieties of arsenic trioxide vaporize at 218°. The vapour density between 500° and 800° corresponds with the molecule  $As_4O_6$ ; and at 1732°, with  $As_2O_3$ . Arsenic trioxide is quite stable if heated in air or oxygen at 100°. Oxidizing agents—like iodine, hydrogen peroxide, nitric acid, and ozone—transform it into arsenic acid. Arsenic trioxide dissolves in hydrochloric acid, forming arsenic trichloride. Reducing agents—stannous chloride—transform it into arsenic and arsine. Arsenic trioxide is very poisonous—0.06 gram is



near the fatal dose for an ordinary man; but the habitual use of small doses makes the system more or less immune to the effects of much larger quantities.

Arsenic trioxide is used in the manufacture of pigments, e.g., *Scheele's green*,  $\text{HCuAsO}_3$ ; *Paris green* or *Schweinfurt green*,  $3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ . These substances are very poisonous and their use as pigments has, consequently, been given up; Paris Green is, however, used as an insecticide and fungicide.

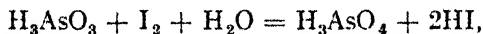
Arsenic trioxide is also used as an insecticide and for rat poison; in preserving the skins of animals and in the manufacture of glass and opaque enamels. It is employed in pyrotechny for the production of "white fire" and its salts are used in medicine (*Fowler's solution*, a weak solution of sodium arsenite, is employed in veterinary surgery), in dyeing and in calico printing. It also finds a use mixed with sodium carbonate for the prevention of boiler incrustations.

### Arsenites

Aqueous solutions of arsenic trioxide exhibit a feebly acidic reaction probably owing to the formation of unstable **arsenious acid**,  $\text{H}_3\text{AsO}_3$ . It differs from the corresponding phosphorous acid in being tribasic. The acid has never been isolated; the solution on concentration deposits crystals of the oxide. Salts are known corresponding to ortho-, pyro-, and meta-arsenious acids— $\text{H}_3\text{AsO}_3$ ,  $\text{H}_4\text{As}_2\text{O}_5$  and  $\text{HAsO}_2$ .

All the arsenites, except the alkali arsenites, are insoluble in water, and they are decomposed by carbonic and hydrosulphuric acids. The soluble arsenites react alkaline owing to hydrolysis: arsenious acid and its salts are reducing agents, but not so powerful as phosphorous acid and the phosphites. Arsenious acid precipitates red cuprous oxide from an alkaline cupric solution; with silver nitrate solution a yellow precipitate of silver arsenite, soluble in acetic acid, is formed. Copper sulphate gives a bright green precipitate of Scheele's green (*vide supra*). When heated, the arsenites are converted into arsenates and free arsenic; and when heated with charcoal, both the arsenates and the arsenites are reduced to elemental arsenic.

Arsenites are oxidized by the halogens, and by bleaching powder, e.g.:



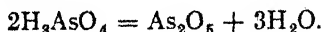
and these reactions are used for their volumetric determination.

### Arsenic Pentoxide, $\text{As}_2\text{O}_5$ , and Arsenates

Arsenic pentoxide cannot be prepared by burning arsenic in oxygen since the product is the trioxide, but can be obtained by the action of oxidizing agents on arsenic trioxide.

By digesting arsenic trioxide with concentrated nitric acid a solution is obtained which, when cold and concentrated, deposits rhombic crystals of  $\text{H}_3\text{AsO}_4 \cdot \text{H}_2\text{O}$ . These melt at about  $36^\circ$ , and when heated

to 100° lose water, leaving a crystalline powder once called **ortho-arsenic acid**,  $\text{H}_3\text{AsO}_4$ . When this arsenic acid is heated to 210° for about two and a half hours, arsenic pentoxide is obtained as a white deliquescent glassy solid:



Unlike phosphorus pentoxide, on heating to a higher temperature (ca. 440°) it breaks down into the trioxide and oxygen.

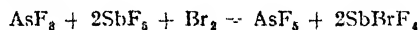
Several arsenates are known, among which may be mentioned: **sodium arsenate**,  $\text{Na}_2\text{HAsO}_4 \cdot 12\text{H}_2\text{O}$ , used in calico printing, and **lead arsenate**,  $\text{PbHAsO}_4$ , used for spraying fruit trees.

The soluble arsenates have an alkaline reaction, and give a reddish-brown precipitate of silver arsenate,  $\text{Ag}_3\text{AsO}_4$ , when neutral solutions are treated with silver nitrate. They also react with ammonium molybdate in presence of nitric acid in a manner similar to the phosphates, giving a yellow precipitate of ammonium arseno-molybdate on boiling.

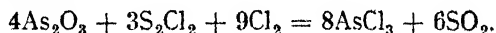
### § 17 Halides and Sulphides of Arsenic

**Arsenic trifluoride**,  $\text{AsF}_3$ , is formed as a volatile fuming liquid, boiling at 63°, when arsenious oxide is distilled with calcium fluoride and sulphuric acid. It is decomposed by water.

**Arsenic pentafluoride**,  $\text{AsF}_5$ , is obtained as a colourless gas by distilling a mixture of the trifluoride with bromine and antimony pentafluoride at a temperature not exceeding 55°:



**Arsenic trichloride**,  $\text{AsCl}_3$ , is formed by the direct union of the elements, or by distilling a mixture of arsenic trioxide with hydrochloric acid, or by heating arsenic trioxide with sulphur chloride in a current of chlorine:



Arsenic trichloride is a heavy, colourless, viscid liquid boiling at 130.2°; which freezes to white needle-like crystals at -18°. It is hydrolysed by water, the reaction being reversible:



It is thus intermediate in behaviour between typical non-metallic chlorides such as phosphorus trichloride, and typical metallic chlorides such as calcium or sodium chlorides.

**Arsenic pentachloride**,  $\text{AsCl}_5$ , is said to be formed when arsenic trichloride is cooled with excess of chlorine; but there is considerable doubt as to its real existence.

**Arsenic tribromide** is a liquid which gives colourless prisms when cooled; and **arsenic tri-iodide** forms orange-red rhombohedral crystals, by direct union of the elements.

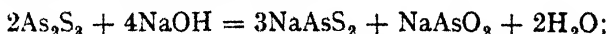
**Arsenic disulphide**,  $\text{As}_2\text{S}_2$ , or more probably,  $\text{As}_4\text{S}_4$ , is found in nature as the mineral *realgar*; and it can be made by heating together

sulphur and arsenic in the right proportions, or by heating arsenic trisulphide with arsenic; or arsenious oxide and sulphur; or distilling a mixture of iron pyrites and arsenical pyrites. Arsenic disulphide is a red brittle vitreous or crystalline solid; it fuses at  $307^{\circ}$  and sublimes unchanged. Heated in air it burns with a blue flame, forming sulphur dioxide and arsenic trioxide. It is used in pyrotechny; for instance, in the manufacture of the so-called "Bengal fire," which is a mixture of realgar, sulphur, and nitre.

### **Arsenic Trisulphide, $\text{As}_2\text{S}_3$**

This sulphide occurs in nature as the mineral *orpiment*—a term derived from the Latin *auri pigmentum*, golden paint. It is employed as a pigment under the name *King's yellow*. Arsenic trisulphide is formed when powdered arsenic and sulphur are heated together in the proportions indicated by the formula,  $\text{As}_2\text{S}_3$ ; and it is also precipitated as a canary-yellow solid when hydrogen sulphide is passed into a solution of an arsenious salt acidified with hydrochloric acid.

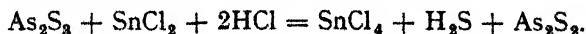
Arsenic trisulphide is a bright yellow solid, insoluble in water, but "soluble" in alkali hydroxides, ammonium carbonate and alkali sulphides. When dissolved in alkali hydroxides, arsenite and thioarsenite (see below) are both formed:



but with the alkali sulphides it forms only **thioarsenites**, which may be regarded as salts of the hypothetical thioarsenious acid,  $\text{H}_3\text{AsS}_3$ . Yellow ammonium sulphide, which contains sulphur in solution, oxidizes arsenic trisulphide to a thioarsenate (see below).

The thioarsenites of the alkalis, alkaline earths, and of magnesium are soluble in water, but decompose on boiling. The solutions are also decomposed by acids with the evolution of hydrogen sulphide, and the reprecipitation of arsenic trisulphide. Hydrogen sulphide will not precipitate arsenic trisulphide from the normal arsenites, and it is only partially precipitated from the primary and secondary arsenites, because soluble thioarsenites are formed. If sufficient acid be present to prevent the formation of the soluble arsenites, precipitation is complete.

**Arsenic pentasulphide**,  $\text{As}_2\text{S}_5$ , can be made by fusing together arsenic trisulphide and sulphur in the right proportions. It is precipitated when a rapid stream of hydrogen sulphide is passed through a cold solution of arsenic acid containing a large excess of hydrochloric acid, or through a strongly acidified solution of a soluble arsenate. Both arsenic tri- and pentasulphides are reduced to the disulphide by a hydrochloric acid solution of stannous chloride:



This explains the formation of the red precipitate which occurs in the detection of arsenic in the presence of tin.

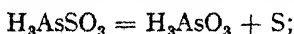
Like the corresponding trisulphide, the pentasulphide will "dissolve" in alkali hydroxides, forming a mixture of arsenate and thioarsenate; and in alkali sulphides, forming thioarsenates only. Acids decompose the thioarsenates with the reprecipitation of the pentasulphide.

Solutions of arsenic acid or of arsenates are reduced slowly by hydrogen sulphide in presence of hydrochloric acid, arsenic trisulphide being ultimately precipitated. It is supposed that the following reactions occur:

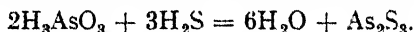
(i) the slow formation of an acid,  $\text{H}_3\text{AsSO}_3$ , intermediate in composition between arsenic acid and thioarsenic acid ( $\text{H}_3\text{AsS}_4$ ):



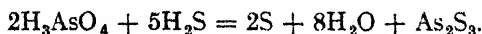
(ii) reduction of this acid to arsenious acid with separation of sulphur:



(iii) decomposition of arsenious acid by hydrogen sulphide:



Summarized, this leads to the equation:



### § 18 Detection of Arsenic

Arsenic is usually detected by means of **Marsh's test**, which depends upon the formation of arsine when nascent hydrogen is produced in a solution containing arsenic.

The standard form of this test is carried out in an apparatus similar to Fig. 35.8.

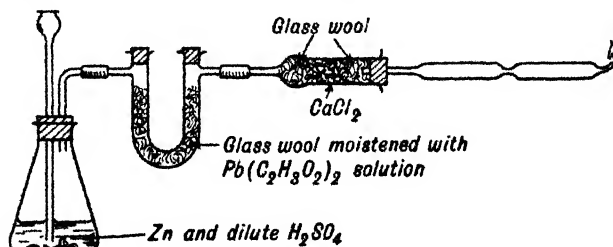


FIG. 35.8.—Marsh's Test

Hydrogen is generated in the small flask from arsenic-free zinc and dilute sulphuric acid and then passed along a glass tube heated at one point by a very small flame. Alternatively, the hydrogen may be generated electrolytically. The solution to be tested for the presence of arsenic is run into the flask, and, if arsenic is present, arsine will be formed. When it reaches the hot part of the tube it is decomposed,

forming a dark shining "mirror" of arsenic just beyond this point. Antimony forms a similar mirror, but can be distinguished by the fact that with it the mirror is nearer to the flame, and it is insoluble in sodium hypochlorite solution, whereas the arsenic mirror is soluble.

**Gutzeit's test**, which is essentially a modification of Marsh's test, is carried out as illustrated in Fig. 35.9.

Hydrogen is produced as before and the suspected solution added. The gases evolved are led up a vertical tube containing a rolled-up lead acetate paper, at the end of which is a sheet of filter paper moistened with mercuric chloride solution, held in position by means of two perforated rubber bungs and a spring clip, as in the diagram. If arsine be present in the gas passing through the paper moistened with mercuric chloride, a yellow stain is produced, which may be compared when produced under standard conditions with standard stains and so used for the estimation of the arsenic present. The exact chemical nature of the yellow compound is uncertain.

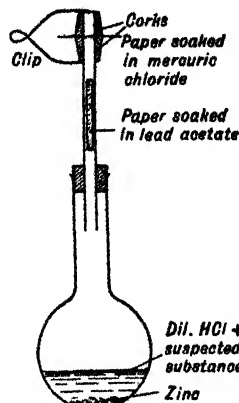


FIG. 35.9.—Gutzeit's Test

**Reinsch's test** depends upon the fact that copper will form copper arsenide when boiled with a hydrochloric acid solution of an arsenic compound. The solution suspected of containing arsenic is added to concentrated hydrochloric acid and a piece of bright copper foil. On warming the copper becomes covered with a dark stain of copper arsenide if arsenic be present. This is then dried and heated in a glass tube in a current of hydrogen, when the arsenic sublimes off the copper and condenses in a mirror on the walls of the tube.

## § 19 Antimony, Sb. History, Occurrence and Preparation

### History

According to Dioscorides and Pliny, *stimmi* and *stibium*—that is, stibnite or antimony sulphide—has long been employed by the women of the East as a medicine, and as an article of toilet for darkening the eyebrows. It is mentioned in this connection in the Old Testament (2 Kings ix. 30; Ezekiel xxiii. 40). Pliny terms it *stibium*, and in a Latin translation of Geber, it is called *antimonium*. Both terms were in common use up to the time of Lavoisier for antimony sulphide.

The derivation of the name *antimony* is uncertain; it has been suggested that it is from *anti* (against) and *moine* (French, a monk), but no weight is attached to this suggestion; the word had also been referred to the Greek *ανθεμώνιον* (*anthemonion*), having reference to the petal-like appearance of the crystals of the naturally occurring mineral (*άνθος*—*ánthos*—a flower).

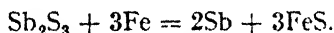
The preparation of the element and the known and imagined properties of antimony were described in the writings attributed to Basi Valentine (supposed to have lived in South Germany in the fifteenth century). The book is entitled *Triumph-Wagen des Antimonii* and is a product of the seventeenth century (cf. page 7).

### Occurrence

Antimony occurs free in small quantities in Borneo and a few other places. It is nearly always accompanied by some arsenic. Antimony occurs combined with oxygen as *antimony bloom*,  $\text{Sb}_2\text{O}_3$ ; and as *antimony ochre*,  $\text{Sb}_2\text{O}_4$ ; combined with sulphur as *stibnite* or *grey antimony ore*,  $\text{Sb}_2\text{S}_3$ ; and as *antimony blende* or *red antimony*,  $\text{Sb}_2\text{S}_2\text{O}$ . It also occurs combined with sulphur and the metals.

### Extraction

The principal source of antimony is stibnite. Good-quality samples are melted by heating with scrap iron, when the iron combines with the sulphur to form a slag of iron sulphide, which floats on the surface of the molten antimony:

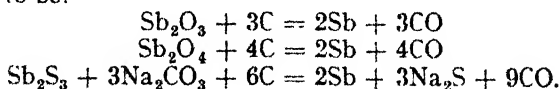


The antimony is purified by remelting two or three times with a little nitre to oxidize contaminating impurities such as lead and sulphur.

With poorer ores the crude sulphide is melted in such a way that the molten sulphide flows away from the less fusible rocky impurities. This process is called **liquation**. The liquated sulphide is then mixed with about half its weight of charcoal and carefully roasted so as to convert the sulphide into oxide:



Part of the antimony oxide condenses in the flues, and a residue of  $\text{Sb}_2\text{O}_4$  and unchanged sulphide remains behind. This is mixed with charcoal and sodium carbonate, and heated in a crucible. The reactions are taken to be:



### § 20 Properties, Uses, etc., of Antimony

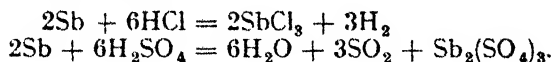
Like phosphorus and arsenic, antimony exists in allotropic modifications; three such are generally distinguished, viz.:

- (i) Crystalline or rhombohedral or  $\beta$ -antimony.
- (ii) Yellow or  $\alpha$ -antimony.
- (iii) Explosive antimony.

The first-named is the variety ordinarily obtained, and referred to as antimony.

It is a silver-white solid with a high metallic lustre and a crystalline (rhombohedral) structure. It is very brittle and can be easily pulverized. Like the non-metals it is a poor conductor of heat, but it has a high specific gravity—6.684. From its physical properties, antimony, like arsenic, would be classed with the metals, but its metallic characters are more pronounced than those of arsenic. Antimony melts at  $630.5^{\circ}$  in an atmosphere of carbon monoxide; and boils at  $1380^{\circ}$ . When the molten element is allowed to cool slowly and partially solidify in a crucible, the uncongealed portion may be poured off. The interior of the crucible is then lined with well-formed rhombohedral crystals of antimony isomorphous with arsenic. The reduced photograph, Pl. 20, illustrates the crystalline surface of a sample of 99.5 per cent antimony. In the act of solidification lead contracts, but antimony expands slightly. Hence molten mixtures of antimony with other metals, when poured into moulds, take the fine and sharp impressions of the mould. For this reason antimony is a constituent of type metal.

Antimony does not tarnish readily on exposure to dry air, but it is oxidized slowly by moist air. Antimony is used to cover other metals like brass and lead alloys. *Antimony black* is finely powdered antimony which is used to coat plaster casts, to make them imitate metals. When heated in air or oxygen, antimony burns with a bright bluish flame, forming antimony trioxide,  $\text{Sb}_2\text{O}_3$ . Antimony combines directly with the halogens. The action is vigorous, and the combining element becomes incandescent. With chlorine, antimony trichloride,  $\text{SbCl}_3$ , is formed. Antimony also unites with sulphur, phosphorus, and arsenic, forming sulphides, phosphides, and arsenides respectively. Dilute hydrochloric and sulphuric acids have little or no action upon antimony, but the more concentrated acids respectively form chloride and an unstable antimony sulphate:



If air be excluded, hydrochloric acid does not attack the pure element. Antimony thus behaves towards these acids like a typical metal. Dilute nitric acid has scarcely any action, but it probably forms an unstable **antimony nitrate**,  $\text{Sb}(\text{NO}_3)_3$ . Concentrated nitric acid does not dissolve the metal but rather oxidizes it to insoluble  $\text{Sb}_2\text{O}_3$  or  $\text{Sb}_2\text{O}_5$ , or a mixture of  $\text{Sb}_2\text{O}_4$  and  $\text{Sb}_2\text{O}_5$ .

**Yellow**, or  $\alpha$ -**antimony** is a metastable form which results when antimony hydride,  $\text{SbH}_3$ , is treated with air at  $-90^{\circ}$ :



This passes into **black antimony** on exposure to light. It is not clear whether black antimony is a definite form or an intermediate form between  $\alpha$ - and  $\beta$ -antimony.

Gore (1855) found that if a current of electricity be passed through a solution of antimony trichloride in hydrochloric acid—using an antimony anode and a platinum cathode—an amorphous powder of specific gravity 5.78 is deposited on the cathode. The cathode has then the appearance of a smooth polished graphite rod. If this deposit be rubbed or scratched, an explosion occurs, the temperature rises to about  $250^{\circ}$ , and 19.6 cal. of heat are evolved per gram of antimony. Clouds of antimony trichloride are given off at the same time. Hence the term **explosive antimony** is applied to this deposit.

Recently, following the work of Krebs *et al.*, considerable doubt has been cast on the view that either  $\alpha$ -antimony or explosive antimony are true allotropes; the former always contains a relatively high proportion of hydrogen and the peculiar properties of the latter are now ascribed to the presence of antimony trichloride.

### Uses

The property possessed by antimony of expanding on solidification leads to its use in a number of alloys. The more important of these are given in Table LVIII.

TABLE LVIII.—ALLOYS OF ANTIMONY

	Sn	Pb	Sb	Cu
Type metal . . . . .	5	75	20	
Stereotype metal . . . . .	2.25	84.21	13.54	
Britannia metal . . . . .	93.3		4.6	2
Pewter . . . . .	83-75	0-20	0-7	0-4
Anti-friction (Babbitt's) metal . . . . .	83.3		8.3	8.3

With copper, a remarkable violet alloy known as *Regulus of Venus* is formed. It is a compound,  $\text{SbCu}_2$ . Modern solders often contain about 2 per cent of antimony. The element is also used in the construction of thermopiles.

Antimony is also used in making paints, e.g., antimony white ( $\text{Sb}_2\text{O}_3$ ) as a substitute for white lead; antimony black as a bronzing powder for metals and plaster; and kermes (see below), a brownish-yellow pigment. It is employed in medicine, in the manufacture of enamels, for colouring pottery and tiles, cloth and paper, and for making of mordants (e.g., the oxychloride). The sulphides are extensively used in the vulcanization of rubber.

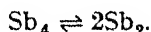
### Atomic and Molecular Weights of Antimony

Consideration of the specific heat of antimony (0.046 at  $186^{\circ}$  and 0.0537 at  $300^{\circ}$ ) together with the molecular weights of volatile compounds such as the trichloride, indicates a value in the neighbourhood of 120 for the atomic weight. The atomic weight has been determined.



for example, by conversion of the metal into its chloride and bromide, followed by estimation of the silver chloride and bromide formed from them. The value obtained by different investigators showed considerable variation, but the value 120.2 was accepted until, in 1923, Aston showed that antimony contains two isotopes of weight 121 and 123, indicating a value for the atomic weight of the ordinary element above 121. Subsequently values were obtained (i) by Hönigschmid and collaborators of 121.76 as the mean of 32 concordant analyses, based on the preparation of pure chloride and bromide; (ii) by Weatherall, of 121.748, using a similar method; (iii) by Willard and McAlpine, who found 121.77. The value at present recommended by the International Committee is 121.76.

The vapour density of antimony at 2000° corresponds with a monatomic molecule; at 1640° it corresponds almost exactly with a molecule  $\text{Sb}_2$ , and at 1380° (the boiling point) very nearly with  $\text{Sb}_3$ . By analogy with arsenic and phosphorus this last result is interpreted as indicating an equilibrium:



### § 21 Hydrides and Oxides of Antimony

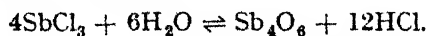
**Antimony hydride, Stibine,  $\text{SbH}_3$ ,** is made in a similar manner to arsenic hydride. It is a colourless poisonous gas with an unpleasant smell. It begins to decompose into its elements even at ordinary temperatures, and sometimes explodes when heated.

It is a powerful reducing agent and may be distinguished from arsenic hydride by its reaction with silver nitrate, with which it gives a precipitate of silver antimonide,  $\text{Ag}_3\text{Sb}$ , and not metallic silver:



**Antimony dihydride,  $\text{Sb}_2\text{H}_2$ ,** is said to be formed as an amorphous grey solid by the decomposition of stibine by sodium hydroxide solution, or by the reduction of the trichloride with zinc and hydrochloric acid. It is very doubtful if it is a definite compound.

**Antimony trioxide, antimonious oxide,  $\text{Sb}_2\text{O}_3$  or  $\text{Sb}_4\text{O}_6$ ,** is made by burning antimony in the air, or by adding hot water to a solution of antimony trichloride or sulphate:



The precipitated oxide is washed with a solution of sodium carbonate to remove the free acid, and finally with water.

Antimonious oxide is a white powder, which volatilizes just over 1500°, when its vapour density corresponds with a molecule  $\text{Sb}_4\text{O}_6$ . The vapour condenses in two distinct forms, isodimorphous with the corresponding crystals of arsenious oxide. Antimonious oxide is very sparingly soluble in water, and the solution has no action on litmus. It is insoluble in dilute nitric and sulphuric acids, but reacts with dilute

hydrochloric acid, forming a solution of the trichloride (q.v.); and with cold concentrated nitric acid, forming **antimony nitrate**,  $\text{Sb}(\text{NO}_3)_3$ , and with hot concentrated sulphuric acid, forming **antimony sulphate**,  $\text{Sb}_2(\text{SO}_4)_3$ . It also forms a solution with tartaric acid and acid potassium tartrate, giving with the latter *tartar emetic* (q.v.) and with alkalis forming salts, e.g.,  $\text{NaSbO}_2 \cdot 3\text{H}_2\text{O}$  derived from the hypothetical **meta-antimonious acid**,  $\text{HSbO}_2$ . **Ortho-antimonious acid**,  $\text{H}_3\text{SbO}_3$ , is obtained as a white solid if sulphuric acid or nitric acid be added to a solution of tartar emetic, and the resulting precipitate dried at  $100^\circ$ . Its formation is probably due to the hydrolysis of the nitrate or sulphate first formed. A **pyroantimonious acid**,  $\text{H}_4\text{Sb}_2\text{O}_5$ , has been reported, but there is some doubt if it has been isolated.

#### Antimony Tetroxide, $\text{Sb}_2\text{O}_4$

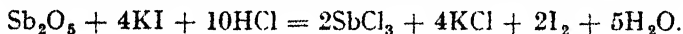
When antimony trioxide is heated in air, it begins to smoulder, forming antimony tetroxide, which is yellow when hot, and white when cold. It is also formed when the pentoxide is heated to a red heat. It has been thought by some to be a mixed anhydride analogous to  $\text{N}_2\text{O}_4$  and  $\text{P}_2\text{O}_4$ ; and on fusion with alkalis it forms salts known as hypoantimonates, e.g.:



**Antimony pentoxide**,  $\text{Sb}_2\text{O}_5$ , is formed by heating pyroantimonous acid (q.v.) to  $300^\circ$ , or by the repeated evaporation of antimony with concentrated nitric acid.

Antimony pentoxide is a straw-yellow powder, almost insoluble in water.

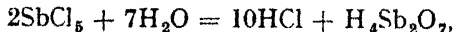
A mixture with water, however, reddens blue litmus. It dissolves in concentrated hydrochloric acid and the mixture has oxidizing properties; for example, it liberates iodine from potassium iodide:



#### Antimonic Acids and Antimonates

**Orthoantimonic acid**,  $\text{H}_3\text{SbO}_4$ , is made by oxidizing antimony trichloride with concentrated nitric acid and diluting the solution with water. A white precipitate is obtained, which yields the ortho-acid when dried over concentrated sulphuric acid. On heating to  $200^\circ$ , it passes into

**Pyroantimonic acid**,  $\text{H}_4\text{Sb}_2\text{O}_7$ , which is also made by the action of nitric acid on antimony at  $100^\circ$ , and most readily by that of hot water on antimony pentachloride:



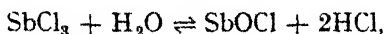
the precipitate formed being dried at  $100^\circ$ . At  $200^\circ$  it is said to pass into *meta-antimonic acid*, and at  $300^\circ$  the pentoxide is formed.

Antimonates are known derived from each of these antimonic acids. Among them may be mentioned **Potassium (dihydrogen) pyroantimonate**,  $\text{K}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ , which is used as a test for sodium since the corresponding **sodium salt** is one of the very few relatively

insoluble salts of sodium. It is made by adding powdered antimony, in small quantities at a time, to four times its weight of fused potassium nitrate. When cold the mass (which may contain the ortho-antimonate) is washed with water, and then boiled with more water, when the dihydrogen salt is formed as a granular powder, sparingly soluble in cold water, but easily soluble in hot.

## § 22 Other Compounds of Antimony

**Antimony trichloride**,  $\text{SbCl}_3$ , is formed by the action of dry chlorine on an excess of antimony, and also by the distillation of an intimate mixture of antimony or antimony sulphide with mercuric chloride. It forms colourless crystals melting at  $73^\circ$  and boiling at  $223^\circ$ . It is highly deliquescent, and is decomposed by cold water, giving the oxychloride:



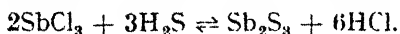
while with hot water the trioxide is precipitated. The **oxychloride**, which is a white powder, was once used in medicine, as a purgative and emetic, under the name of "powder of Algaroth."

**Antimony pentachloride**,  $\text{SbCl}_5$ , is formed when chlorine is passed through fused antimony trichloride. It is a colourless or slightly yellow liquid which crystallizes at  $2.8^\circ$ , fumes in air, and boils with partial dissociation into antimony trichloride and chlorine at  $140^\circ$ . In this it resembles phosphorus pentachloride.

Antimony also forms a crystalline trifluoride, tribromide and triiodide by direct combination of the elements; a pentafluoride, which is a liquid at ordinary temperatures, is also known.

**Antimony trisulphide**,  $\text{Sb}_2\text{S}_3$ , occurs in two forms: an orange form and a black form. The latter, known as stibnite, is the principal ore of antimony.

The black form is made by heating antimony with sulphur; while the orange form is precipitated when hydrogen sulphide is passed through an acidified solution of antimony trichloride:



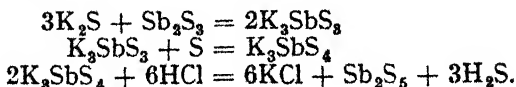
The orange form passes into the black form on heating.

Antimony trisulphide is used in the manufacture of safety matches, fireworks, etc.; whilst a mixture of antimony trisulphide and trioxide, known as *Kermes mineral*, is used in medicine and is made by boiling antimony trisulphide with sodium or potassium carbonate.

Antimony trisulphide reacts with alkalis and alkali sulphides in a similar manner to arsenic trisulphide, forming *thioantimonites* and *thioantimonates*.

**Antimony pentasulphide**,  $\text{Sb}_2\text{S}_5$ , is made by the action of hydrogen sulphide on a mixture of antimony pentachloride with a little water. It is also obtained by acting upon the trisulphide, along with sulphur,

with potassium hydroxide, and decomposing the potassium thioantimonate so formed with dilute hydrochloric acid:

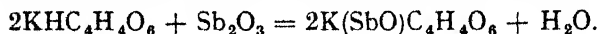


Antimony pentasulphide is a reddish-yellow solid which combines with alkali sulphides, forming thioantimonates. **Schlippe's salt** is sodium thioantimonate,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ . Antimony pentasulphide is used in the vulcanization of rubber.

#### **Tartar Emetic. Potassium Antimonyl Tartrate,**



Tartar emetic is made by boiling a solution of "cream of tartar," i.e., potassium hydrogen tartrate, with antimony trioxide. On cooling the concentrated solution it separates in octahedral crystals:



Tartar emetic is the most important salt of antimony in commerce. It is used in medicine in small doses as an emetic; large doses are poisonous. It is also used for the treatment of some tropical diseases such as kala-azar. Large quantities are used as a mordant.

#### **Detection of Antimony**

Antimony is detected by the formation of an orange precipitate of the sulphide when hydrogen sulphide is passed through a not-too-acid solution of an antimony salt. This precipitate can be distinguished from arsenic sulphide by reason of its insolubility in concentrated ammonium carbonate solution. A 2 per cent solution of "cupferron" gives a yellowish-white precipitate with antimonious compounds, but no precipitate with antimonic compounds.

Marsh's test can also be applied to the detection of antimony as indicated on page 843.

Reinsch's test (page 843) can also be applied to the detection of antimony. It is distinguished from arsenic by the facts that the sublimate of antimony trioxide is non-crystalline and hydrogen sulphide gives an orange-red precipitate when passed through a solution of the oxide in dilute hydrochloric acid.

### **§ 23 Bismuth, Bi. History, Occurrence and Preparation**

#### **History**

Metallic bismuth was described in the writings ascribed to Basil Valentine under the name *marcasite*, a name formerly used vaguely for almost any ore with a metallic appearance. Most of the writers of the seventeenth century confused bismuth with antimony or zinc.

J. H. Pott (1739) first demonstrated the characteristic properties of bismuth, and its reactions were later studied by C. J. Geoffroy (1753) and T. Bergmann (1780). The name bismuth is supposed to be derived from the German "Weissmuth" (white matter).

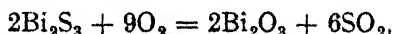
### Occurrence

Bismuth is found in many localities—Bolivia, Saxony, etc.—in a fairly pure condition in a free state. It also occurs combined with sulphur as *bismuth glance*,  $\text{Bi}_2\text{S}_3$ ; with tellurium as *tetradymite*,  $\text{Bi}_2\text{Te}_3$ ; and with oxygen as *bismite* or *bismuth ochre*,  $\text{Bi}_2\text{O}_3$ . *Bismuthite* is a hydrated carbonate. Most of the bismuth in commerce comes from Bolivia, and some from Australia and Bohemia.

In the United States much bismuth is now obtained as a by-product in the refining of lead and other metals.

### Extraction

The principal ores are the sulphide and bismuthyl carbonate. The former, after concentration by washing or magnetic separation, is roasted so as to form the oxide:



which is then reduced by heating with charcoal in a reverberatory furnace. The bismuth recovered from lead smelting, etc., occurs in the anode slimes of electrolytic refining processes (e.g., Bett's process, page 792). These residues are fused with sodium hydroxide and sodium carbonate, and the resulting material cast into slabs which are refined electrolytically, using a bath of bismuth chloride and hydrochloric acid. A very pure metal can be obtained in this way; the purification of cruder samples is effected by fusion on an inclined plate in contact with air. Bismuth is only slowly oxidized at the melting point, whereas the impurities are usually readily oxidized or volatilized.

### Properties

Bismuth is a greyish-white solid resembling antimony, but it has also a faint reddish tinge. It is hard, brittle, lustrous and crystallizes readily; and, like antimony, it expands on solidification. It melts at  $271.3^\circ$ , and if the molten metal be allowed partly to solidify in a crucible, and the uncongealed liquid poured off (as in the preparation of monoclinic sulphur—page 475) the crucible will be found lined with rhombohedral crystals of the element. Bismuth boils at  $1420^\circ$ , and it distils in an atmosphere of hydrogen if heated over  $1100^\circ$ . It is a very bad conductor of heat, its specific gravity is high (9.8) and it is strongly diamagnetic (i.e., *repelled* by an ordinary magnet). The metallic properties are more pronounced than with either antimony or arsenic, and whereas in arsenic non-metallic properties predominate, in bismuth the metallic properties are most pronounced. Bismuth is oxidized only

superficially on exposure to the air, but if heated in air it burns, forming the oxide  $\text{Bi}_2\text{O}_3$ . It decomposes steam at a red heat, but is not affected by cold air-free water. It unites directly with the halogens and with sulphur. It is but slightly attacked by hydrochloric acid and by hot concentrated sulphuric acid, and is readily attacked by dilute and concentrated nitric acid, forming the corresponding salts.

### Uses

Bismuth is used in the manufacture of alloys, in particular of fusible metals. Thus *Newton's metal* (tin, 3; lead, 5; bismuth, 8) melts at  $94.5^\circ$ ; *Rose's fusible metal* (tin, 1; lead, 1; bismuth, 2) melts at  $93.75^\circ$ ; and *Wood's fusible metal* (tin, 1; lead, 2; cadmium, 1; bismuth, 4) melts at  $60.5^\circ$ . Fusible alloys, which melt at about  $100^\circ$ , are used in automatic sprinklers; less fusible alloys are used for making safety plugs in steam boilers, fuses in electrical connections, and in fire alarms. The gas pipe which enters a building can also be fitted with a piece of fusible alloy so that if a fire breaks out the alloy will melt, choke the gas pipe, and stop the flow of gas. Fireproof doors can also be kept open by fusible plugs which allow the doors to close automatically in the event of fire. The oxide or nitrate is used in making some kinds of optical glass, and in the decoration of pottery with lustres. The basic nitrate was once used as a cosmetic, but is now largely displaced by the cheaper zinc oxide. Some bismuth compounds, especially the carbonate, are used medicinally.

Bismuth is also used in the construction of thermopiles.

### Atomic and Molecular Weights

The atomic weight of bismuth is seen to be in the neighbourhood of 208 from its specific heat ( $0.0303$  at  $18^\circ$ ), and the vapour density of volatile compounds such as the chloride. Among the methods employed for its accurate determination are conversion of the metal into the oxide and vice versa; conversion of the metal and the oxide into the sulphate; and the formation of silver chloride and bromide from bismuth chloride and bromide. Honigsmid, by the last method, obtained values between 208.98 and 209.00, and considers the most probable value to be 209.00, which is the value recommended by the International Committee.

The vapour density of bismuth between  $1600^\circ$  and  $1700^\circ$  is about 158 ( $\text{H}_2 = 1$ ), corresponding to a mixture of  $\text{Bi}_2$  and Bi molecules. At  $2000^\circ$  the molecule is monatomic.

## § 24 Hydride and Oxides of Bismuth

### Bismuth Hydride, $\text{BiH}_3$

This substance was first prepared by Paneth and co-workers in 1918. They obtained it in very small quantities by the action of dilute hydrochloric or sulphuric acid on a bismuth-magnesium alloy. Its formation was first detected

by the use of the radioactive isotopes of bismuth, radium C and thorium C, which can be detected in very small amounts. It is an exceedingly unstable gas, but can be condensed in liquid air. It decomposes very readily on heating, with separation of bismuth.

### Bismuth Oxides

Four oxides of bismuth have been described, viz.:

Bismuth suboxide, or monoxide,  $\text{BiO}$ ,  
 Bismuth trioxide,  $\text{Bi}_2\text{O}_3$ ,  
 Bismuth dioxide or tetroxide,  $\text{Bi}_2\text{O}_4$ ,  
 Bismuth pentoxide,  $\text{Bi}_2\text{O}_5$ .

The first-named is somewhat doubtful.

**Bismuth suboxide**,  $\text{BiO}$ , is said to be formed when the trioxide is reduced with carbon monoxide, or when bismuth oxalate is heated. It is a black powder, which has been thought by some to be a mixture of bismuth and bismuth trioxide.

### Bismuth Trioxide, $\text{Bi}_2\text{O}_3$

This oxide is formed when bismuth is heated in air, or when the hydrated oxide, carbonate or nitrate is calcined. The other oxides also pass into the trioxide when heated in air. It is a cream-coloured powder, which is not acted upon by water. It is readily reduced to the metal when heated with carbon or hydrogen. It exhibits marked basic properties, for it reacts with acids to form salts. It forms a series of hydrates,  $\text{BiO} \cdot \text{OH}$ ,  $(\text{HO})_2\text{BiOBi}(\text{OH})_2$  and  $\text{Bi}(\text{OH})_3$ , which can be obtained by pouring an acid solution of bismuth nitrate into excess of aqueous ammonia, when the trihydrate is formed. This loses water progressively on gentle heating. These hydrates do not exhibit any acidic properties.

### Bismuth Dioxide, or Tetroxide, $\text{Bi}_2\text{O}_4$

If chlorine be passed into a boiling aqueous solution of potassium hydroxide in which bismuth trioxide is suspended, a dark chocolate-brown precipitate is formed:



The precipitate is washed with water and dilute nitric acid, and dried at  $180^\circ$ . It appears to be a mixture of hydrated bismuth tetroxide,  $\text{Bi}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , with variable amounts of the pentoxide. In some respects this oxide resembles antimony tetroxide, but its mode of formation and many properties are like those of lead dioxide. When heated to  $200^\circ$  it decomposes into the trioxide. With hydrochloric acid it gives chlorine and the trichloride, and with oxyacids it gives oxygen and a bismuth salt.

### Bismuth Pentoxide, $\text{Bi}_2\text{O}_5$ . Bismuthic Acid

If the action of chlorine on an alkaline suspension of bismuth trioxide be continued for a long period the precipitate becomes scarlet red, and has the composition of **potassium metabismuthate**,  $\text{KBiO}_3$ . If this precipitate be washed and boiled for a short time in dilute nitric acid, scarlet-red **meta-bismuthic acid** is obtained, and when this is dried, bismuth pentoxide is formed as an unstable brown powder. When heated above  $120^\circ$ , it decomposes and bismuth trioxide is formed. With hydrochloric acid and oxyacids it furnishes bismuth salts and

chlorine or oxygen; thus resembling antimony pentoxide in behaving as a basic peroxide. The formation of bismuthates shows that it also exhibits feeble acidic properties.

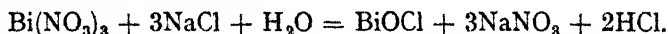
### § 25 Other Compounds of Bismuth

**Bismuth carbonate**, bismuthyl carbonate,  $(\text{BiO})_2\text{CO}_3$ , is precipitated by addition of carbonate or bicarbonate solutions to bismuth nitrate. It is a basic carbonate, the normal carbonate being unknown; but it is the only carbonate formed by elements of Group V.

**Bismuth chloride**,  $\text{BiCl}_3$ , is formed by the direct action of chlorine on bismuth; by heating bismuth with mercuric chloride; by the action of concentrated hydrochloric acid on bismuth trioxide; and by the action of *aqua regia* on bismuth. Bismuth trichloride is a white crystalline mass, deliquescent in air. It melts at  $230^\circ$  and boils at  $447^\circ$ . Its vapour density 164 corresponds with the formula  $\text{BiCl}_3$ . When bismuth trichloride is dissolved in a little water it forms a syrupy liquid, but with an excess of water, a white precipitate of bismuth oxychloride,  $\text{BiOCl}$ .

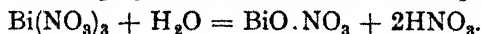
This property is used as a test for bismuth in qualitative analysis.

**Bismuth oxychloride**, bismuthyl chloride,  $\text{BiOCl}$ , is obtained as above from the trichloride, or by the interaction of solutions of sodium chloride and bismuth nitrate:



It differs from the oxychlorides of arsenic and antimony in that it is not decomposed by water; and from antimony oxychloride in being insoluble in tartaric acid. It has been used as a pigment under the name of "pearl white."

**Bismuth nitrate**,  $\text{Bi}(\text{NO}_3)_3$ , can be made by the action of nitric acid on bismuth itself, or on the trioxide or carbonate. It is a colourless crystalline deliquescent substance, soluble in water. With a large excess of water, it forms **bismuth subnitrate** which is used in medicine, and was at one time employed as a constituent of face-powder:



**Bismuth sulphide**,  $\text{Bi}_2\text{S}_3$ , occurs native as *bismuth glance* and is formed as a dark brown precipitate when hydrogen sulphide is passed through a solution of a bismuth salt acidified with hydrochloric acid. It differs from the trisulphides of arsenic and antimony in not exhibiting such marked acidic properties; thus it does not form solutions with alkali hydroxides or hydrosulphide, although it does react to some extent with alkali sulphides.

### § 26 The Elements of Sub-Group VA

#### Vanadium, V

##### History

Del Rio, in 1801, expressed the opinion that a Mexican ore which he analysed contained a new metal which he called "crythronium"—from the Greek *ερυθρός*



(*erythros*), red—because it furnished red salts when treated with acids. Del Rio abandoned his opinion when Collet-Descostils, four years later, claimed that the supposed new metal was an impure chromium oxide. In 1830 N. G. Sefström described a new mineral which he found in some Swedish iron ores, and suggested for it the name "vanadium"—from "Vanadis," a Scandinavian goddess. Immediately afterwards, F. Wöhler, 1831, established the identity of Sefström's "vanadium" with Del Rio's "erythronium." F. Wöhler had also found something strange in a Mexican lead ore from Zimapan, before Sefström's announcement, and put it aside for future examination.

J. J. Berzelius, 1831, investigated vanadium, and he appears to have been under the impression that the oxide VO was the metal itself. H. E. Roscoe, in 1867, isolated the metal and established its relationship with the nitrogen family of elements.

### Occurrence

Vanadium does not occur free, but is widely distributed in many rocks. The principal ores are *carnotite* (potassium uranyl vanadate),  $2\text{U}_2\text{O}_5 \cdot \text{V}_2\text{O}_5 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$ ; *patronite*, an impure vanadium sulphide; and *vanadinite*,  $\text{Pb}_3(\text{VO}_4)\text{Cl}_2$ , which is mined in the Peruvian Andes. The ashes of some Peruvian coals are said to contain up to 48 per cent of vanadic oxide. Small quantities occur in iron ores, and traces occur in many British fireclays and granitic rocks.

### Extraction

For commercial purposes vanadium is not required in the pure metallic state; most of it is marketed in the form of a ferro-vanadium alloy containing 30 to 40 per cent of vanadium.

The ores are fused with sodium carbonate and nitrate, and sodium vanadate is formed. This is extracted with water and treated with an ammonium salt, which gives an orange-coloured precipitate of ammonium meta-vanadate,  $\text{NH}_4\text{VO}_3$ . When this salt is heated, more or less impure vanadium pentoxide remains.

The ferro-vanadium is obtained from the pentoxide (or crude vanadates, such as iron vanadate) by reduction of a mixture of the vanadium compound, iron ore or scale, lime or fluorspar and coke in an electric furnace. As an alternative the Goldschmidt thermite process can be used.

Pure vanadium is difficult to obtain even on a small scale on account of the high temperature necessary, and the tendency to re-oxidation. The metal has been obtained by reduction of the pentoxide by the "thermite" method, using *mischmetal* (page 760) in place of aluminium. Vanadium is notable for the number of valency states which it exhibits; thus oxides and halides corresponding to valencies of 2, 3, 4 and 5 are known. The compounds in which vanadium exhibits valencies less than 5 are usually powerful reducing agents.

Vanadium forms at least four oxides, viz.:

- Hypovanadous oxide, VO or  $\text{V}_2\text{O}_2$ ,
- Vanadous oxide,  $\text{V}_2\text{O}_3$ ,
- Hypovanadic oxide,  $\text{VO}_2$  or  $\text{V}_2\text{O}_4$ ,
- Vanadic oxide (vanadium pentoxide),  $\text{V}_2\text{O}_5$ .

In addition a monoxide  $\text{V}_2\text{O}$  has been reported, though its existence is doubtful.

**Hypovanadous oxide**, VO or  $\text{V}_2\text{O}_2$ , is made by the reduction of higher oxides with potassium. It is a black powder which was at one time mistaken for the element. It reacts with acids forming lavender-coloured solutions of hypovanadous salts, from which caustic alkalis precipitate **hypovanadous hydroxide**,  $\text{V}(\text{OH})_2$ , one of the most powerful reducing agents known.

**Vanadous oxide, vanadium trioxide**,  $\text{V}_2\text{O}_3$ , is made as a black powder by reducing the pentoxide with hydrogen. It burns in air to the pentoxide and only reacts with acids with difficulty. The vanadous salts when obtained are green in solution.

**Hypovanadic oxide**,  $\text{VO}_2$  or  $\text{V}_2\text{O}_4$ , is made by reducing the pentoxide with

sulphur dioxide. It is an amphoteric oxide; thus with alkali hydroxides it forms hydrovanadates, e.g., sodium hypovanadate,  $\text{Na}_2\text{V}_4\text{O}_{18}$ , while vanadyl salts result with acids, e.g., vanadyl chloride,  $\text{VOCl}_2$ . The vanadyl salts give blue solutions.

**Vanadium pentoxide**,  $\text{V}_2\text{O}_5$ , results from the oxidation of vanadium compounds in general. It is a yellowish-red powder, sparingly soluble in water, which with alkalis gives rise to a series of vanadates analogous to the phosphates, e.g.,  $\text{Na}_3\text{VO}_4$ ,  $\text{NaVO}_3$ ,  $\text{Na}_4\text{V}_2\text{O}_7$ .

The basic properties of vanadium oxides become less and less pronounced as the proportion of oxygen increases. The higher oxides exhibit acidic as well as basic properties. The element also forms a series of chlorides:  $\text{VCl}_2$ ,  $\text{VCl}_3$ , and  $\text{VCl}_4$ . The existence of  $\text{VCl}_1$  is doubtful. There is also a series of vanadyl compounds or oxychlorides— $(\text{VO})_2\text{Cl}$ ,  $\text{VOCl}$ ,  $\text{VOCl}_2$ , and  $\text{VOCl}_3$ . Unlike nitrogen and phosphorus, vanadium is undoubtedly a metal. As in the case of phosphorus, the element, if heated to a high temperature, burns to the pentoxide,  $\text{V}_2\text{O}_5$ . The melting point of the metal is  $1730^\circ$ ; it boils about  $3000^\circ$ .

Vanadium is used in making special steels because very small quantities of vanadium produce a remarkable refinement of the "grain" with consequent increase of tensile strength, ductility and fatigue limit. Chrome-vanadium steel is used for motor-vehicle springs and other components subjected to alternations of stress and, in amounts up to about 1.5 per cent, vanadium is an essential constituent of high-speed steels. (Cf. page 880.)

Vanadium pentoxide is used as a catalyst in the oxidation of naphthalene and in the manufacture of sulphuric acid (modified contact process, page 503). Compounds of vanadium are also employed in the manufacture of ink, in dyeing, as accelerators in the drying of paint and varnish, in insecticides, photographic chemicals, therapeutic preparations and in glass manufacture.

### History of Niobium and Tantalum

In 1801 C. Hatchett analysed some chromium minerals from Connecticut, and found an earth hitherto unknown. He named the mineral "columbite," after the place of its origin, and the element was designated "columbium." A year later, 1802, A. G. Ekeberg found a new element in some Finnish minerals resembling columbite. To this he gave the name "tantalum," from "Tantalus" of Grecian mythology, in allusion to the "tantalizing" difficulties he encountered in dissolving the mineral in acids. In 1844 H. Rose noticed two new elements in a sample of columbite from Bodenmais: one, tantalum, is similar to Ekeberg's tantalum; and the other has been called "niobium," from Niobe, the mythological daughter of Tantalus. Hatchett's "columbium" was probably a mixture of both tantalum and niobium. The term "columbium" is still applied to Rose's niobium, particularly in the U.S.A.

### Niobium, Nb, or Columbium, Cb, and Tantalum, Ta

These two elements are found associated in the isomorphous minerals *tantalite*,  $\text{Fe}(\text{TaO}_3)_2$ ; and *columbite* or *niobite*,  $\text{Fe}(\text{NbO}_3)_2$ . One or both of the elements occur in several rare earths—monazite, and yttriotantalite—and also in tinstone, pitchblende, wolfram, and many other minerals.

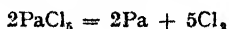
On account of the occurrence of the lanthanide contraction (page 153) the atomic volumes of niobium and tantalum are almost identical; consequently, their chemical properties are very closely alike. Niobium forms a mono-, di-, and a penta-oxide; and tantalum a di- and a penta-oxide. Niobium forms both a tri- and a pentachloride, while tantalum forms the pentachloride. Both elements exhibit feeble base-forming qualities, and their chief compounds are the niobates and the tantalates. The elements are produced when the chlorides are reduced in a current of hydrogen. Tantalum forms a series of complex salts with alkaline fluorides. Thus,  $\text{K}_2\text{TaF}_7$  is formed in rhombic needles when a solution of tantalum acid in hydrofluoric acid is treated with potassium fluoride. The sparing solubility of this salt in hydrofluoric acid enables tantalum to be separated from niobium. Niobium metal melts at about  $2415^\circ$ , tantalum at about  $3000^\circ$ .

Tantalum was formerly used for the filaments of electric lamps, but it has now been superseded by tungsten for this purpose. It is used as an electrode in alternating-current rectifiers, and in the manufacture of surgical and dental instruments on account of its resistance to chemical attack, and the hardness of the surface which can be produced by suitable heat treatment. The carbides of niobium and tantalum are used in conjunction with tungsten carbide in the production of certain classes of steel-cutting tools and dies.

#### Protoactinium, Pa

The principal investigations of protoactinium have been connected with its radioactive properties.

Protoactinium was discovered by Soddy in 1917 and, independently at about the same time, by Hahn and Meitner. It has been separated from pitchblende residues (after the extraction of radium and uranium) in relatively large amounts (*ca.* 0.5 gm.) by von Grosse (1935). The element itself has also been isolated by von Grosse by bombarding the oxide ( $\text{Pa}_2\text{O}_5$ ) on a copper target with a stream of electrons, in a high vacuum, the metal being obtained as a shiny, partly sintered, metallic mass which is stable in air. It has also been obtained by decomposition of the chloride, in a high vacuum, on an electrically heated tungsten wire:



Chemically protoactinium appears to resemble tantalum although the pentoxide, a heavy white powder, is slightly basic and resembles thorium dioxide; thus it reacts with warm concentrated sulphuric acid; but is not affected by fused potassium carbonate. In this it resembles its horizontal neighbours in the Periodic Table.

The atomic weight of protoactinium was investigated by von Grosse from the ratio  $\text{K}_2\text{PaF}_7 : \text{Pa}_2\text{O}_5$ , the value 230.6 being obtained. The principal isotope has the mass number 231; this isotope is noteworthy in being fissionable by neutrons of relatively low energy. The atomic weight of protoactinium being less than that of thorium these two elements thus constitute another reversed pair like argon and potassium, and iodine and tellurium.

### § 27 The Relationships of the Group V Elements

In this group the relationship between the "typical" elements and the elements of the B sub-group is much more marked than with the A sub-group. This is usual in the later groups of the Periodic Table and is in harmony with present-day views concerning the electronic configurations of the atoms. These configurations are indicated in Tables LIX and LX. From these figures it is evident that the members of the A sub-group are properly regarded as transition elements, since the penultimate electron group is incomplete, and is in process of filling up. On the other hand the elements of the B sub-group have the penultimate group complete. It is also clear that the five elements nitrogen, phosphorus, arsenic, antimony and bismuth are alike in having complete penultimate electron groups, and an identical configuration of the outermost electron group. The close resemblance between vanadium, niobium and tantalum is also indicated, likewise the extent of the resemblances and differences to be anticipated between these three and the other five elements. Thus, as transition elements, they are characterized by very variable valency; the formation of highly coloured ions; they are also paramagnetic, and have

marked catalytic power. The variability of valency depends upon the fact that some of the electrons of the incomplete penultimate group can be detached almost as easily as the outermost and, consequently, leads to the expectation that the resemblance to the nitrogen-bismuth series will be mainly confined to the compounds of highest valency (five) in each case.

TABLE LIX

Element	Electrons in orbits																
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p	6d	7s
Vanadium .	2	2	6	2	6	3	2										
Niobium .	2	2	6	2	6	10	2	6	4		1						
Tantalum .	2	2	6	2	6	10	2	6	10	14	2	6	3	2			
Protoactinium .	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	4	1

TABLE LX

Element	Electrons in orbits														
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p
Nitrogen . . .	2	2	3												
Phosphorus . . .	2	2	6	2	3										
Arsenic . . . .	2	2	6	2	6	10	2	3							
Antimony . . . .	2	2	6	2	6	10	2	6	10		2	3			
Bismuth . . . .	2	2	6	2	6	10	2	6	10	14	2	6	10	2	3

Turning now to the general characteristics of the two sections of the group, the properties of nitrogen, phosphorus, arsenic, antimony and bismuth show a gradual transition from the non-metallic nitrogen to the metallic bismuth. The apparent chemical inactivity of nitrogen is in striking contrast with the activity of phosphorus; and the volatility and solubility of the oxides and acids of nitrogen are in similar contrast with the corresponding compounds of phosphorus. The relationship of the physical properties is indicated in Table LXI.

The gradual transition of non-metals into metals with increasing atomic weight is brought out very clearly in this family group. The changes in the melting and boiling points are not so regular as the other properties, but this may be related to the fact that phosphorus, arsenic, and antimony have four-atom molecules, whereas bismuth, like nitrogen, has probably a two-atom molecule. The heat of combination of the different elements with hydrogen shows a somewhat similar gradation:  $\text{NH}_3$ , + 12 cal.;  $\text{PH}_3$ , + 4.9 cal.;  $\text{AsH}_3$ , - 44.2 cal.;  $\text{SbH}_3$ , - 86.8 cal. Ammonia is a relatively strong base, phosphine a feeble base, while arsine and stibine do not show basic qualities. Hence, as the atomic weight increases, the basicity of the hydride

decreases. This is shown by the formation of the ammonium and phosphonium salts, and the non-existence of the arsonium and stibium compounds. The resemblances between nitrogen, phosphorus, arsenic and antimony as foreshadowed by the similarities between their trihydrides is accentuated by a comparison of the compounds  $N(C_2H_5)_3$ ,  $P(C_2H_5)_3$ ,  $As(C_2H_5)_3$ ,  $Sb(C_2H_5)_3$ , and the analogy becomes still further pronounced in comparing  $N(C_2H_5)_4OH$ ,  $P(C_2H_5)_4OH$ ,  $As(C_2H_5)_4OH$ ,  $Sb(C_2H_5)_4OH$ , for these bodies are so surprisingly similar that they are almost indistinguishable from one another.

TABLE LXI.—PROPERTIES OF THE NITROGEN-PHOSPHORUS FAMILY

	Nitrogen	Phosphorus	Arsenic	Antimony	Bismuth
Atomic weight .	14.008	30.975	74.91	121.76	209.00
Specific gravity	(solid) 1.026	1.82–2.31	4.7–5.7	6.684	9.8
Atomic volume	13.7	about 15	13 to 16	18	21.3
Melting point	–209.9°	44.1°	[814°]	630.5°	271.3°
Boiling point	–195.8°	282°	[610°]	1440°	1420°

While phosphoric oxide is volatile and stable, the corresponding pentoxides of arsenic, antimony and bismuth are resolved by heat into the corresponding trioxides and oxygen. Phosphorus pentoxide yields a whole series of polybasic acids, but nitrogen pentoxide gives but one monobasic acid,  $HNO_3$ ; the corresponding salts are also in strong contrast, for the nitrates are nearly all soluble in water, while the normal, pyro- and metaphosphates are nearly always sparingly soluble. Similarly with the trioxides, strict analogy is absent. The oxy-acids diminish in strength during the passage from nitric to phosphoric, to arsenic, to antimonic, to bismuthic acid. The acidic properties of the oxides likewise diminish from the strongly acid nitrogen and phosphorus acids to the feebly acidic oxides of arsenic, antimony and bismuth. The basic property first appears with arsenic and becomes stronger during the passage to antimony and to bismuth. The trichloride of nitrogen is very unstable, while with bismuth the trichloride is quite stable. The boiling points of the trichlorides increase with increasing atomic weights of the elements, thus:  $NCl_3$  boils at 70°;  $PCl_3$ , 73.5°;  $AsCl_3$ , 130.2°;  $SbCl_3$ , 223°; and  $BiCl_3$ , at 447°. The halogen compounds of nitrogen and phosphorus are completely hydrolysed by water; arsenic trichloride is also hydrolysed by water, but it can exist in solution in the presence of hydrochloric acid. Antimony and bismuth halides are incompletely hydrolysed by water.

In contrast with many of the foregoing properties, the elements of the A sub-group have high melting and boiling points (see Table LXII); their oxides are extremely difficult to reduce, and are all typical metals both in appearance and behaviour. Further, they do not form hydrides. In contrast, the elements of both groups form pentoxides which are acidic. Strongly so in the light elements, becoming less so

with increasing atomic number and atomic weight, until bismuth pent-oxide is only just acidic.

TABLE LXII.—PROPERTIES OF THE VANADIUM FAMILY

	Vanadium	Columbium, or Niobium	Tantalum
Atomic weight . . .	50.95	92.91	180.95
Colour . . . . .	Silvery metal	Steel-grey metal	Iron-grey metal
Specific gravity . . .	5.96	8.6	16.6
Atomic volume . . .	9.3	13.3	23
Melting point . . .	1730°	2415°	3000°

Thus, in general, the resemblance between the A and B sub-groups, which becomes steadily more marked in passing across the Periodic Table from Group I to Group IV, becomes less so in Group V; and this reversal of tendency will be seen to continue in proceeding to Groups VI and VII where the resemblance becomes still less noticeable.

## CHAPTER 36

# SELENIUM, TELLURIUM AND POLONIUM

### § 1 Group VIB of the Periodic Table

GROUP VI comprises the elements oxygen and sulphur, together with chromium, tungsten, molybdenum and uranium on the one hand; and selenium and tellurium on the other. (The radio-element polonium also belongs to this latter sub-group; but so far it has been obtained in such minute quantities that its chemical and physical properties have hardly been studied. Here, as is usual in the later part of the Periodic Table, the elements in the short periods are more closely related to the B sub-group than to the A, and so it is found that sulphur, selenium and tellurium form a well-defined family.

Sulphur forms a link between oxygen and selenium and tellurium, but it resembles the former less than the latter elements. Oxygen has been discussed in Chapter 21, and sulphur in Chapter 24. The relationships of Group VI as a whole are described at the end of Chapter 37.

### § 2 Selenium, Se

Selenium is a rather uncommon element, although small quantities are often found associated with sulphur and sulphides, e.g., in pyrites. Hence, it is found in the "flue dust" of the pyrites burners in the manufacture of sulphuric acid. It was discovered by J. J. Berzelius, in 1817, and named from the Greek *σεληνή* (*selene*), the moon, owing to its resemblance to tellurium, which had been discovered a few years before, and named after the earth (see below).

The principal source of selenium is now the anode mud obtained in the electrolytic refining of copper (page 649). This mud is roasted in air, which causes the selenium dioxide formed to be volatilized off. It is then dissolved in hydrochloric acid and reduced with sulphur dioxide which causes the precipitation of selenium. A little selenium remains unoxidized after the roasting, and is recovered, along with tellurium (see below), by heating the residue with sodium hydroxide and nitrate, whereby sodium selenite and tellurite are formed. These are extracted with water, and the solution acidified, so causing the precipitation of tellurium dioxide. This is removed and selenium precipitated with sulphur dioxide as before.

Selenium shows considerable resemblance to sulphur, and, like it, exists in several allotropic forms. The most stable form is a grey crystalline variety; there are also several orange or red crystalline modifications, and at least two amorphous forms. Selenium melts at 220° and boils at 685°, giving a dark red vapour. Measurements of the vapour density of selenium indicate that the molecule is diatomic up to about 1000°; at higher temperatures dissociation into atoms occurs.

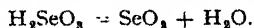
One of the most interesting properties of selenium is the increase in its electrical conductivity on exposure to light and vice versa, a phenomenon which was discovered by W. Smith in 1873. The change is proportional to the intensity of the light, and red and orange light are the most active. It was formerly supposed that the effect depended upon the change from a feebly conducting to a good conducting allotropic form of selenium, but it is now thought to be due to the light causing emission of electrons, thus bringing about increase in conductivity. This behaviour has been made use of in photo-electric cells in various optical and electrical appliances such as telephotography, photometry and detecting devices

Selenium is mainly used in the glass industry for neutralizing the green tinge of ordinary glass, and for making ruby glass, and in the manufacture of red pigments for enamelled iron. It is also being used in increasing amounts in the rubber industry and in the preparation of pigments and paints, e.g., cadmium selenide. Certain organic derivatives are employed as photographic sensitizers and for toning, and selenobenzamide is used in froth flotation processes. Selenium is also now being employed, in conjunction with iron, for the rectification of alternating currents. It is used in organic chemistry for dehydrogenation.

**Atomic weight of selenium.** The value at present recommended for the atomic weight of selenium is 78.96. This is based on the work of Hönigschmid (1933) who obtained it as the mean of eleven experiments in which silver selenide was synthesized quantitatively from metallic silver. The same value was also suggested by Aston from determination of the relative abundance of the isotopes of selenium.

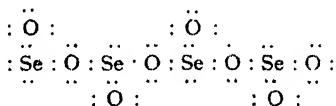
**Selenium hydride** is a gas of obnoxious odour made by the action of dilute hydrochloric acid on ferrous selenide. It resembles hydrogen sulphide, but is more poisonous, and less stable. It is soluble in water, burns in air to selenium dioxide and water, and acts with solutions of metallic salts in a similar manner to hydrogen sulphide.

**Selenium dioxide**,  $\text{SeO}_2$ , is formed when selenium burns in dry oxygen, and by evaporating a solution of selenious acid prepared as described below:



It is a white crystalline solid, which sublimes at  $300^\circ$ , and combines with water forming selenious acid. It is used as an oxidizing agent in organic chemistry.

Crystals of selenium dioxide have been shown, by X-ray examination, to consist of chains of alternate oxygen and selenium atoms with another oxygen atom attached to each selenium atom. The electronic structure is represented thus:



**Selenium trioxide**,  $\text{SeO}_3$ , has been prepared (Rheinboldt, Hessel and Schwenzer, 1930) by the action of oxygen on selenium under the influence of a high-frequency discharge. It is a white, very hygroscopic solid.

**Selenious acid**,  $\text{H}_2\text{SeO}_3$ , is made by the action of nitric acid on selenium:



It is a colourless, crystalline solid, soluble in water; the solution resembles sulphurous acid. It decomposes on heating, and is readily reduced to selenium, e.g., by sulphur dioxide. On oxidation, e.g., by chlorine or bromine, selenic acid is formed.

**Selenic acid**,  $\text{H}_2\text{SeO}_4$ , is made by oxidation of aqueous selenious acid by means of chlorine:



On cautious evaporation of the solution, crystals of the acid can be obtained. It resembles sulphuric acid in many respects, particularly in its vigorous action with water. It is, however, a weaker acid than sulphuric, and is much more readily decomposed by heat, passing at temperatures much below its boiling point into selenium dioxide and oxygen:



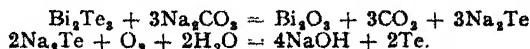
The selenates are very similar to the sulphates, with which they are isomorphous.

Selenium forms compounds of the type  $\text{SeX}_4$  with fluorine, chlorine and bromine; it also forms a very stable hexafluoride, but no compounds of selenium and iodine are known.



### § 3 Tellurium, Te

Tellurium, like selenium, is not a plentiful element, although it is widely distributed in small amounts. It occurs as tellurides such as *tetradymite*,  $\text{Bi}_2\text{Te}_3$ , and, with selenium, is found in the anode mud from electrolytic copper refining. This is the principal source of tellurium. It is obtained from the mud as tellurium dioxide, as described under selenium, and is reduced to the element by roasting with coal or charcoal, or by passing sulphur dioxide into its solution in hydrochloric acid. It can also be made from tetradymite by fusion with sodium carbonate, followed by oxidation of the sodium telluride thus formed by passing air through its aqueous solution:



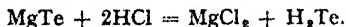
Tellurium was discovered in 1782 by Muller von Reichenstein, and named by Klaproth in 1798 from the Latin *tellus*, the earth. It exists in at least two allotropic forms. The stable form is a grey, crystalline solid with a metallic lustre; the other form is amorphous. Tellurium resembles both sulphur and selenium in chemical properties, but the hydride is even more unstable than hydrogen selenide and the dioxide is amphoteric. It burns in air to the dioxide, and is attacked by chlorine. It is unaffected by acids which are not oxidizing agents, nitric and sulphuric acids oxidize it.

The addition of tellurium to lead has been suggested, since it increases its resistance to chemical attack and improves its tensile strength, and lead containing 0.05 per cent of tellurium is used for the sheaths of electric cables. It has also been used for electroplating silver for the production of a dark finish, and as an addition to copper (Cf. page 652.)

#### Atomic Weight of Tellurium

From the time when Mendeléeff first enunciated the Periodic Law until Moseley's work on atomic numbers, the atomic weights of iodine and tellurium occasioned difficulty. For all determinations of these quantities resulted in values for tellurium higher than those for iodine. These, if followed in drawing up the Periodic Table, would require iodine to come before tellurium, and thus put these two elements in obviously unsuitable places; iodine with sulphur and selenium, and tellurium with the halogens. Mendeléeff himself rightly reversed this order, but predicted that further investigation would show one or both of these atomic weights to be wrong. This prediction has not been fulfilled; the values at present recommended by the International Committee being 127.61 for tellurium (based on some sixty sets of experiments, particularly those of Hönigschmid) and 126.92 for iodine. The true explanation of these facts was furnished by the work of Moseley, who showed that the position of an element in the Periodic Table is determined by its atomic *number* and not by its atomic weight; and of Aston who found that tellurium consists of several isotopes of masses 122, 123, 124, 125, 126, 128 and 130, the last two being present in by far the largest proportion, thus giving tellurium an atomic weight substantially greater than that of iodine which is a "pure" element of mass 127. (See also Chapter 10, pages 140-3.)

**Hydrogen telluride**,  $\text{H}_2\text{Te}$ , is obtained by the action of dilute hydrochloric acid upon zinc or magnesium telluride:



It is usually contaminated with hydrogen when prepared in this way; it can be purified by condensation in a freezing mixture, since it boils at  $-1.8^\circ$ . It is a colourless gas, with an evil smell; it is even more unstable than hydrogen selenide, decomposing at ordinary temperatures on exposure to light. In the main it resembles hydrogen selenide.

**Tellurium dioxide**,  $\text{TeO}_2$ , is obtained, like selenium dioxide, by burning the element in air or oxygen, or by oxidation with nitric acid. It is a colourless solid,

very sparingly soluble in water, and the solution is neutral to litmus. It reacts with alkali hydroxide solutions, forming solutions of *tellurites*; it also exhibits feeble basic properties forming, for example, a basic nitrate,  $2\text{TeO}_3 \cdot \text{HNO}_3$ .

**Tellurium trioxide**,  $\text{TeO}_3$ , is obtained as an orange-yellow powder by heating telluric acid to dull redness. It is insoluble in water, with which it does not recombine to form telluric acid.

**Telluric acid**,  $\text{H}_6\text{TeO}_6$ , is formed by dissolving tellurium in a mixture of nitric and hydrochloric acids, which yields tellurous acid; and then oxidizing by adding chloric acid in small portions. The resulting solution is evaporated *in vacuo*, when the acid crystallizes out and may be recrystallized from water. It is a colourless crystalline solid of the composition  $\text{H}_6\text{TeO}_6$  and was formerly considered to be the hydrate  $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ . It is now believed to be not a hydrate, but the true ortho-acid  $\text{H}_6\text{TeO}_6$ , a belief which is confirmed by the preparation of the compound  $\text{Ca}_3\text{TeO}_6$ , and by the molecular weight of the acid in solution. It is a very weak acid, which differs considerably from sulphuric acid. It is reduced to tellurium by sulphur dioxide.

The tellurates somewhat resemble the selenates, but, unlike them, are not isomorphous with the sulphates, and do not form alums.

Tellurium forms halides of the type  $\text{TeX}_4$  with all four halogens; in addition a hexafluoride  $\text{TeF}_6$  is known, and the dihalides  $\text{TeCl}_2$  and  $\text{TeBr}_2$  have been reported.

#### § 4 Polonium

Polonium was discovered by Madame Curie, who isolated it from pitchblende. It is a breakdown product of radium but, since its half-life period is only 138.3 days, it cannot accumulate in the mineral to any great extent. (The equilibrium quantity is about 0.004 mgm. per ton.) The best source of the element is the decayed radon from hospitals where this gas is used for the treatment of cancer.

Polonium forms a hydride,  $\text{PoH}_2$ , and several oxides;  $\text{PoO}$ ,  $\text{Po}_2\text{O}_3$ ,  $\text{PoO}_2$ , and  $\text{PoO}_3$  have been reported. It also forms a sulphide (in which it differs from selenium and tellurium); the chlorides  $\text{PoCl}_2$  and  $\text{PoCl}_4$  have also been described.

## CHAPTER 37

# CHROMIUM, MOLYBDENUM, TUNGSTEN AND URANIUM

### § 1 Sub-group VIA of the Periodic Table

THE sub-group comprises the four elements chromium, molybdenum, tungsten and uranium, which exhibit among themselves a considerable amount of resemblance in their properties, and to a lesser extent justify classification along with the elements of Group VIB, oxygen, sulphur, etc. As in Group VA, there are important horizontal relationships.

### § 2 Chromium, Cr. History, Occurrence and Extraction

#### History

In 1762 J. G. Legmann, in a letter to the naturalist G. L. L. de Buffon, described a new mineral from Siberia. We now know this mineral to be crocoisite, or lead chromate. Both L. N. Vauquelin and Macquart, in 1789, failed to recognize in the mineral a new element, and both reported lead, iron, alumina, and a large amount of oxygen. However, in 1797, L. N. Vauquelin re-examined the mineral and concluded that the lead must be combined with a peculiar acid which he considered to be the oxide of a new metal. This he called chromium—from the Greek *χρῶμα* (*chroma*), colour—because its compounds are all coloured. In 1798 L. N. Vauquelin detected the new element in spinel and in smaragdite, and F. Tassaert found chromium in chrome iron ore in 1799.

#### Occurrence

Metallic chromium does not occur free in nature. It occurs combined with oxygen in *chrome ochre*, which is chromium sesquioxide,  $\text{Cr}_2\text{O}_3$ , associated with more or less earthy matters. *Chromite*,  $\text{Fe}(\text{CrO}_2)_2$ , is the chief ore of chromium. It also occurs as lead chromate in *crocoisite*,  $\text{PbCrO}_4$ . Traces occur in many minerals—emerald, jade, serpentine, etc.

#### Extraction of Metallic Chromium

The principal source of chromium is chrome iron ore (chromite). Chromium comes on to the market principally as sodium or potassium chromate and dichromate, made from the ore, as described on page 870.

Metallic chromium is made commercially by the "thermite"

process (cf. page 745) and by reduction of chromic oxide by means of the theoretical amount of silicon in an electric arc furnace. Some quicklime is also added to form a slag with the silica produced:



For the former process an intimate mixture of chromium sesquioxide and aluminium powder is placed in a refractory-lined container. A mixture of sodium or barium peroxide and aluminium powder is placed over this; a piece of magnesium ribbon is stuck into the latter mixture and a layer of powdered fluorspar placed over all. The crucible is embedded in sand and the magnesium ribbon ignited. When the flame reaches the peroxide mixture, the aluminium is oxidized with explosive violence; the heat of combustion of the aluminium in this ignition mixture starts the reaction between the chromic oxide and aluminium, and it rapidly spreads through the whole mass. The chromium formed is melted and sinks to the bottom of the crucible, and the alumina forms a slag of artificial corundum:

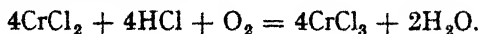


### § 3 Properties, Uses and Atomic Weight of Chromium

Chromium is a bluish-white metal, capable of taking a very high polish. The pure metal is relatively soft, but as usually obtained chromium is among the hardest of the common metals on account of the presence of small amounts of carbon. It has a high melting point,  $1800^\circ$ . Under ordinary conditions it is stable in air, but it is superficially oxidized when heated in air or oxygen. When heated to  $2000^\circ$  in oxygen it burns with great brilliance. It retains a brilliant finish when exposed to all normal atmospheric corroding agents, including rain, snow and sea-water, hydrogen sulphide, sulphur dioxide and sulphur compounds generally. It is attacked by dilute hydrochloric and sulphuric acids, slowly in the cold, more rapidly on heating, forming blue solutions of chromous salts and hydrogen:



These blue solutions rapidly turn green on exposure to the air owing to the formation of chromic salts:



Concentrated sulphuric acid attacks it, yielding sulphur dioxide and chromic sulphate. Dilute nitric acid does not attack the pure metal and when placed in contact with concentrated nitric acid, chromium becomes inert or *passive*; it is no longer attacked by acids which dissolve it under normal conditions. This phenomenon is further considered under iron (page 916).

### Uses

The most important use of chromium is probably the production of special steels. It is added to the steel in the form of an alloy with iron known as *ferrochrome* (containing 40 to 80 per cent of chromium), made from chromite either by the aluminothermic process, or by reduction with carbon in an electric furnace. There are three main types of *stainless steel*, viz., one containing 13 per cent of chromium and 0.1 to 0.4 per cent of carbon (used for cutlery); one with 17 per cent of chromium and 2 per cent of nickel; and the *staybrite* type with 18 per cent of chromium and 6 per cent of nickel, with or without small additions of titanium, silicon or niobium. A chrome steel with 1 to 1½ per cent of carbon and 2½ to 4 per cent of chromium is so hard that it cannot be worked by ordinary hardened tool steels so that it is drill-proof. It is used in the manufacture of burglar-proof safes, stamp-mill shoes, etc. Chrome-vanadium steel is very hard and strong, and is now being used for gears, springs, axle-shafts, locomotive wheels, etc. It has the very valuable property that its characteristics can be varied to a surprising extent by heat treatment. Chrome-nickel steels are used for armour plates; and chrome-tungsten and chrome-molybdenum steels are used for high-speed tools.

*Nichrome* is an important alloy, containing approximately 11 to 25 per cent of chromium, and 50 to 70 per cent of nickel (the rest usually being iron), which is remarkably resistant to atmospheric corrosion, even at high temperatures. It is hence used for the windings of electric fires and for similar purposes. Its special properties are probably the result of a protective oxide layer which has almost the same coefficient of expansion as the parent metal and is therefore coherent. *Stellite*, an alloy of chromium, cobalt and tungsten, is used for surgical instruments, and some motor-car parts. It has also been suggested for the manufacture of tools, and possesses remarkable resistance to corrosion.

Chromium is now widely used as a plating metal on account of its remarkable resistance to corrosion, and the high protective power of thin layers.

For chromium plating the conditions require careful control, although the exact details vary somewhat in different works. The baths used always contain chromium in both the hexavalent and trivalent conditions, e.g., chromium trioxide (250 grams per litre) and chromium sulphate (3 grams per litre), using a lead anode. Small quantities of other sulphates, such as cobalt, nickel, zinc or cadmium, are sometimes added, as these improve the "throwing power" of the bath; and a temperature of 40° is often employed as this results in the formation of a very hard, coherent deposit. In plating iron it is usual to put on a layer of copper or nickel, sometimes both, before the chromium.

Of chromium compounds, chromite is used in making the hearths of steel furnaces since it can be used as a neutral refractory material between the basic (magnesian) bricks and acidic (siliceous) bricks. Chromite bricks are not injured by contact with basic, nor with acid

bricks; whereas acidic and basic bricks, when heated in contact with one another, are likely to fuse at the surfaces of contact owing to the formation of fusible silicates. The bricks are very refractory—softening between  $2000^{\circ}$  and  $2100^{\circ}$ —and do not crack by sudden heating and cooling.

Potassium and sodium chromates are used in dyeing; in the manufacture of pigments (chrome yellow, chrome red, Guignet's green, etc.); in tanning leather, etc.

Chromium salts are also used as colouring agents in the manufacture of glass and pottery, and are used as mordants in dyeing.

### Atomic Weight

The atomic weight of chromium is seen to be in the neighbourhood of 52 from the vapour densities of volatile compounds, such as chromyl chloride and the value of its specific heat (0.12).

The most accurate experimental determinations of the combining weight have been made by preparing pure silver chromate and dichromate, followed by reduction with sulphur dioxide and in other ways, and the precipitation of the silver, as silver chloride, with all possible precautions. In this way, Baxter obtained the value 52.01 for the atomic weight of chromium and this is the value at present recommended by the International Committee.

### § 4 Oxides and Hydroxides of Chromium

Chromium forms three well-defined oxides, viz.:

Chromous oxide,  $\text{CrO}$ ,

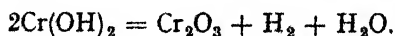
Chromium sesquioxide or chromic oxide,  $\text{Cr}_2\text{O}_3$ ,

Chromium trioxide,  $\text{CrO}_3$ .

In addition, several other oxides have been reported, and regarded as chromium chromates, e.g.,  $\text{Cr}_3\text{O}_6$  or  $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$  and  $\text{Cr}_8\text{O}_{21}$ , or  $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$ , as well as  $\text{CrO}_5$ ,  $\text{CrO}_2$ , but their individual existence is somewhat doubtful. In addition, the blue solution obtained by the action of hydrogen peroxide on a solution of a chromate, in presence of acid, is now believed to contain chromium pentoxide,  $\text{CrO}_5$  (*vide* page 326).

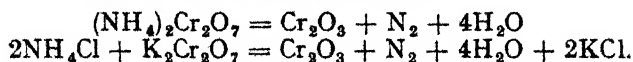
**Chromous oxide**,  $\text{CrO}$ , is obtained as a black powder by warming chromium amalgam with dilute nitric acid. It is not attacked by nitric acid, but reacts with dilute sulphuric and hydrochloric acids. It is reduced by hydrogen at  $1000^{\circ}$ , whereas chromic oxide is not affected by hydrogen at  $1300^{\circ}$ .

**Chromous hydroxide**,  $\text{Cr}(\text{OH})_2$ , is obtained by the action of alkali hydroxide solutions on solutions of chromous salts. It is a yellowish-brown precipitate which rapidly oxidizes in air, and which decomposes, on heating, into chromic oxide, hydrogen and water:



**Chromium Sesquioxide, Chromic Oxide,  $\text{Cr}_2\text{O}_3$** 

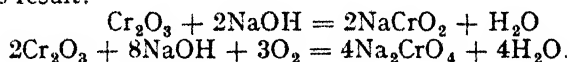
This oxide is obtained when chromic hydroxide is heated, and also when ammonium dichromate, or a mixture of potassium dichromate and ammonium chloride, is treated similarly:



In the latter case, the green residue is washed with water till free from potassium chloride, and dried.

Chromic oxide is a green powder, which is used as a pigment. Thus, *Guignet's green*, for instance, is made by calcining potassium dichromate with boric acid, etc. Chromic sesquioxide, in an extremely fine state of subdivision, appears to be crimson, for if an intimate mixture of stannic oxide, or zinc oxide, or alumina, with a very small proportion of chromic oxide, be heated to a high temperature in an oxidizing atmosphere a red powder is obtained. There is some evidence to show that the red colour is not caused by the formation of a chemical compound, and that the "chrome-tin" colour is related to purple of Cassius (q.v.). The "chrome-tin" crimson is used for colouring pottery, glazes, etc.

Chromic oxide is a basic oxide, and forms salts with acids. When, however, it has been calcined at a high temperature it only dissolves in acids very slowly. It also appears to exhibit acidic properties, for, when fused with alkalis, it forms *chromites*, and if air be allowed access or an oxidizing agent such as potassium chlorate be present, yellow chromates result:



It is thus an amphoteric oxide.

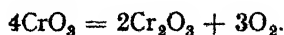
**Chromic hydroxide**,  $\text{Cr}(\text{OH})_3$ , separates as a bluish-green, gelatinous precipitate when ammonia or alkali hydroxide solution is added to a green chromic salt. When freshly precipitated, it reacts readily with acids, forming chromic salts; but after standing for some time in contact with dilute alkali, its properties change and it then only reacts with difficulty. Another variety, probably a hydrated form, results when alkali is added to solutions of violet chromic salts. Similarly, when freshly precipitated, chromic hydroxide goes into solution in alkali hydroxide solution, possibly with the formation of chromites; although it has been suggested that these are solutions of colloidal chromium hydroxide. On heating, chromium hydroxide loses water and chromic oxide remains. In presence of alkali solutions, chromic hydroxide is readily oxidized to chromates by chlorine or bromine.

**Chromium trioxide**,  $\text{CrO}_3$ , is obtained in long, scarlet, needle-like crystals when a concentrated solution of potassium dichromate is treated with concentrated sulphuric acid and cooled:



The crystals are filtered on glass-wool, washed with concentrated nitric acid to remove sulphates and sulphuric acid, and dried in a current of warm air.

Chromium trioxide forms deep red, very deliquescent, prismatic needles. It can be volatilized at about  $110^\circ$  and melts at  $196^\circ$  with some decomposition. When heated to  $250^\circ$ , it rapidly decomposes into chromic oxide and oxygen:



It is very soluble in water, and the solution probably contains several of the polychromic acids (see below).

Chromium trioxide is a vigorous oxidizing agent owing to the readiness with which it seems to part with oxygen to form chromic oxide,  $\text{Cr}_2\text{O}_3$ . Thus, alcohol dropped on to the oxide takes fire; when ammonia gas impinges on the crystals, the reduction takes place with incandescence; paper is charred at once; carbonaceous matter is oxidized to carbon dioxide.

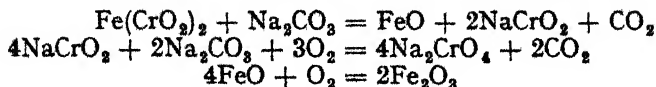
### Polychromic Acids

The solution of chromium trioxide in water is strongly acid and deep orange-red in colour, and probably contains several *condensed* chromic acids, e.g., dichromic acid,  $\text{H}_2\text{Cr}_2\text{O}_7$ ; trichromic acid,  $\text{H}_2\text{Cr}_3\text{O}_{10}$ ; and tetrachromic acid,  $\text{H}_2\text{Cr}_4\text{O}_{13}$ . The chromate ion,  $\text{CrO}_4^{--}$ , is apparently not stable in presence of acid (or hydrogen ion). Salts corresponding to these acids are known. Thus potassium dichromate (described below) is the most important compound of chromium; by treating it with chromium trioxide, **potassium trichromate**,  $\text{K}_2\text{Cr}_3\text{O}_{10}$ , is formed; and by treating the trichromate with concentrated nitric acid, **potassium tetrachromate**,  $\text{K}_2\text{Cr}_4\text{O}_{13}$ , results. These polychromates can be crystallized out. These salts, and the polychromic acids from which they are derived, result from the condensation of two, three or four molecules of chromic acid, with elimination of water.

The addition of alkali to any of these polychromates reconverts them into normal chromates; water hydrolyses them to dichromates. This phenomenon of condensation occurs with a number of oxyacids, e.g., boric, iodic and phosphoric acids, and particularly with molybdic and tungstic acids (pages 878 and 880).

**Potassium chromate and dichromate** are the most important compounds of chromium, and are manufactured from chrome iron ore via the sodium salts. The ore is finely ground and mixed with soda-ash (anhydrous sodium carbonate) and quicklime and then roasted in an oxidizing atmosphere in a reverberatory or rotating furnace. The roasted mass is then mixed with water, when the ferric oxide remains behind and sodium chromate passes into solution. The reactions which take place are probably:



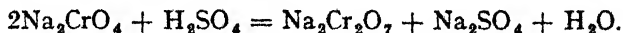


or, combined into a single equation:



The presence of quicklime serves to keep the mass porous and so assist the access of air.

The sodium chromate is extracted with water from the melt obtained as above and concentrated sulphuric acid is added to the solution to convert it into sodium dichromate:



Sodium sulphate crystallizes out (with  $10\text{H}_2\text{O}$ ) and the clear solution is decanted off, and evaporated in iron pans. When it has attained a specific gravity of 1.7, it is filtered from the further crop of sodium sulphate which has separated, and then allowed to cool. Crystals of **sodium dichromate**,  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , separate on standing. This salt is made on a large scale and is preferred to the potassium compound for many purposes, both on account of its cheapness and greater solubility (100 grams of water dissolve 109 grams of the salt at  $15^\circ$ ), but it has the drawback of being deliquescent. Its chemical properties closely resemble those of potassium dichromate.

**Potassium dichromate**,  $\text{K}_2\text{Cr}_2\text{O}_7$ , is made by mixing hot concentrated solutions of sodium dichromate and potassium chloride. Sodium chloride is precipitated and removed and then, on cooling, potassium dichromate separates out:

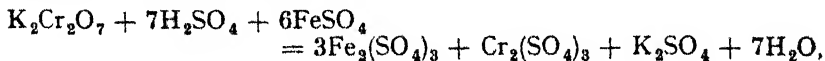


Potassium dichromate forms large red triclinic crystals, which melt at  $400^\circ$ . It is moderately soluble in cold water (100 grams of water dissolve 10 grams of the salt at  $15^\circ$ ) and easily soluble in hot water (100 grams of water dissolve 102 grams at  $100^\circ$ ). It is thus readily purified by recrystallization from water.

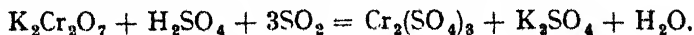
Potassium dichromate is an important oxidizing agent; and its solutions are used for this purpose in volumetric analysis. In acid solution, one molecule of potassium dichromate will furnish three atoms (i.e., *six equivalents*) of available oxygen, as indicated in the equation:



It will thus oxidize six atoms (or six equivalents) of ferrous iron:



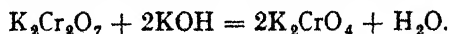
or three molecules (six equivalents) of sulphur dioxide:



Potassium dichromate will also oxidize the halogen acids to the free halogens, and is used as an oxidizing agent in organic chemistry.

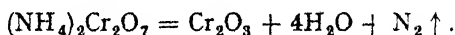
**Sodium chromate**,  $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ , can be crystallized out of the solution obtained by extracting the product of heating chromite and soda-ash. It forms large transparent yellow crystals and closely resembles the potassium salt except that it is deliquescent.

**Potassium chromate**,  $\text{K}_2\text{CrO}_4$ , can be made from chromite in the same way as sodium chromate; or by the addition of potassium hydroxide solution to a solution of potassium dichromate:



It forms lemon-yellow crystals which are isomorphous with those of potassium sulphate. It is very soluble in water (100 grams of water dissolve 60 grams at  $10^\circ$ ) and is stable in the absence of reducing agents, which convert it into chromic hydroxide or oxide. Acids convert chromates into dichromates; a change which is accompanied by a change in colour of the solution from yellow to orange. This change is reversible in the sense that alkalis convert dichromates into chromates.

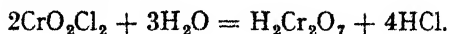
**Ammonium dichromate**,  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ , is formed when aqueous solutions of ammonia and chromic acid are mixed. When the solid is heated, nitrogen, water, and a voluminous mass of chromic oxide (resembling green tea) are obtained:



This reaction, if started at one point in a quantity of the salt, will rapidly spread right through the whole mass; if the salt is confined it becomes explosive.

### Chromyl Chloride, $\text{CrO}_2\text{Cl}_2$

When potassium dichromate, a soluble chloride and strong sulphuric acid are heated in a retort, chromyl chloride, an acid chloride analogous to sulphuryl chloride, distils over. The most satisfactory method of preparation is that described by H. D. Law and F. Mollwo Perkin. Chromium trioxide is dissolved in rather more than the equivalent quantity of concentrated hydrochloric acid, and concentrated sulphuric acid is added in small quantities, the mixture being cooled after each addition. After standing the lower layer of chromyl chloride is run off by means of a tap funnel. Chromyl chloride is a deep-red liquid which boils at  $117^\circ$ , and which is hydrolysed by water into hydrochloric acid and, probably, dichromic acid:



These reactions are used as a test for chlorides since neither bromides nor iodides form similar compounds. Consequently, if a mixture suspected to contain a chloride be distilled with sulphuric acid and potassium dichromate, and a deep-red distillate results which with

water gives a solution which, after neutralization, responds to the tests for chromates, the presence of chlorides may be inferred.

When a concentrated solution of potassium dichromate in hydrochloric acid is allowed to crystallize, yellowish-red crystals of **potassium chlorochromate** ( $\text{KCrO}_3\text{Cl}$  or  $\text{KO} \cdot \text{CrO}_2\text{Cl}$ ) are formed. This is derived from the unknown *chlorochromic acid*, which is constituted analogously to chlorosulphonic acid. It decomposes on heating into potassium dichromate, chromic oxide, chlorine and oxygen:



### § 5 Chromous Salts

Chromium forms two series of salts in which the element behaves as a basic metal, derived respectively from chromous and chromic oxides.

The chromous salts are blue in colour, or give blue solutions, and are powerful reducing agents. They are rapidly oxidized on exposure to the air, forming chromic salts.

**Chromous chloride**,  $\text{CrCl}_2$ , is made by heating chromic chloride in a current of hydrogen. As thus prepared, it is a white, crystalline compound. It dissolves in water, forming a blue solution; in solution, chromous chloride can also be made by reducing chromic chloride by means of zinc and hydrochloric acid.

Blue needles of  $\text{CrCl}_2 \cdot 4\text{H}_2\text{O}$  are precipitated when chromous acetate is dissolved in concentrated hydrochloric acid, in an atmosphere of hydrogen, and the solution cooled in ice while a current of hydrogen chloride is passed in.

**Chromous sulphate**,  $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ , is obtained in blue crystals, isomorphous with ferrous sulphate, by dissolving chromium, or chromous acetate, in dilute sulphuric acid and cooling the solution.

**Chromous acetate**,  $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_2$ , can be obtained by adding a strong solution of chromous chloride (made as above by reduction of chromic chloride with zinc and hydrochloric acid) to a saturated solution of sodium acetate. It is then precipitated in red crystals which can be filtered off and dried *in vacuo*. It is fairly stable, and may be used for the preparation of other chromous salts.

### § 6 Chromic Salts

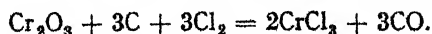
The chromic salts are derived from chromic oxide (or hydroxide) and while in some respects they exhibit the properties to be expected of the salts of a trivalent radical, and thus resemble the corresponding derivatives of aluminium and iron, they show also some marked peculiarities.

Thus, most of them exist in at least two forms, a violet form and a green form; and some are found in three varieties. Further, in the green forms they are found to be only partly ionized, and some are known which are not ionized at all.

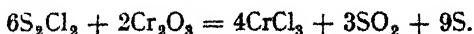
The explanation of these facts has been suggested by Werner to be similar to that put forward by him to account for the existence and properties of the remarkable complex compounds which chromium, platinum and other transitional metals form with ammonia, cyanides, etc. These, and Werner's theory of their constitution, are discussed in Chapter 39 (page 946).

**Chromic Chloride,  $\text{CrCl}_3$** 

The anhydrous salt is made by passing chlorine over either chromium metal, or a mixture of chromic oxide and carbon heated to redness:



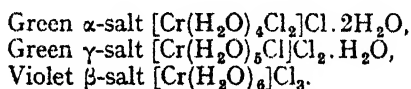
It is also obtained by the action of sulphur chloride vapour on chromic oxide:



It is a pinkish-violet solid, which is virtually insoluble in water, unless a mere trace of a chromous salt be present, when it dissolves easily.

Three crystalline hydrates are known, all having the empirical composition  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ . Two of these are green and are known as the  $\alpha$ - and  $\gamma$ -salts, and one is violet (the  $\beta$ -salt).

The violet  $\beta$ -salt is made by passing hydrogen chloride into a saturated solution of the oxide in hydrochloric acid at a low temperature (under  $10^\circ$ ); at a higher temperature the violet solution becomes green, and when saturated with hydrogen chloride deposits green rhombic crystals of the  $\alpha$ -salt. The other green salt—the  $\gamma$ -salt—is obtained by treating the mother liquor from the violet crystals with ether, saturated with hydrogen chloride. These three salts are remarkable in that when freshly prepared solutions are treated with silver nitrate, with the  $\alpha$ -salt one-third of the total chlorine present is precipitated as silver chloride; with the  $\gamma$ -salt two-thirds, and with the violet  $\beta$ -salt the whole is precipitated. Werner symbolizes these results in the formulae:



In these formulae, the atoms or molecules inside the square brackets are believed to be attached to the chromium atom by covalent or co-ordinate links and are therefore non-ionizable, while those outside the brackets are attached by electrovalent and hence ionizable valencies (cf. pages 155 and 947).

The violet  $\beta$ -salt is practically insoluble in water unless a trace of chromous chloride be present.

**Chromic sulphide,  $\text{Cr}_2\text{S}_3$ ,** is not obtained when hydrogen sulphide is passed into a solution of a chromic salt, as it is completely hydrolysed and the hydroxide is precipitated. It is made by heating chromic oxide to redness in a stream of hydrogen sulphide or by heating chromium in sulphur vapour. It is curious that, although it is not decomposed by water, it is not formed when hydrogen sulphide is passed into a solution of a chromic salt; chromic hydroxide is precipitated instead. It is a brownish-black amorphous powder.

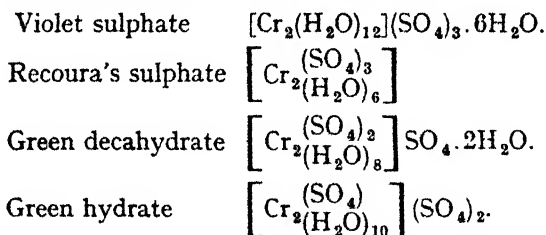
**Chromic Sulphate,  $\text{Cr}_2(\text{SO}_4)_3$** 

The anhydrous salt is obtained in bluish-red crystals by dehydration of a hydrate in air at  $400^\circ$  or in a stream of carbon dioxide at about  $300^\circ$ . It is insoluble in water and acids.

Chromic sulphate forms a variety of hydrates containing varying amounts of water; both green and violet forms are known; and the different varieties have varying proportions of their sulphate radicals precipitated by barium chloride.

A violet sulphate, which behaves normally with barium chloride, is obtained by dissolving chromic hydroxide in the calculated quantity of warm sulphuric acid and allowing the green solution which results to stand for a week. It then becomes bluish-violet in colour and deposits violet crystals, said to have the composition  $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ .

Alternatively, a green hexahydrate, sometimes known as *Recoura's sulphate*, which is obtained by saturating chromic acid solution at  $-4^\circ$  with sulphur dioxide, gives, when freshly prepared, a solution which forms no precipitate with barium chloride. Another green hydrate, containing ten molecules of water, obtained when the green solution formed by reducing chromic acid with sulphur dioxide at  $0^\circ$  and evaporating *in vacuo*, has one-third of its "sulphate" precipitated by barium chloride. A green hydrate is known from which barium chloride precipitates two-thirds of the "sulphate." According to Werner's theory these sulphates are formulated:



There is much in the chemistry of these salts, however, which is obscure and merits further investigation.

**Chrome Alum, Potassium Chromium Alum,  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$** 

Chrome alum is readily prepared by reducing potassium dichromate solution, acidified with sulphuric acid, by means of sulphur dioxide and similar reducing agents:



It is obtained commercially as a by-product in the course of the manufacture of alizarin, for which anthracene is oxidized to anthraquinone by potassium dichromate and sulphuric acid.

Chrome alum crystallizes in deep violet octahedra, isomorphous with the other alums. It is fairly soluble in water (100 grams of water

dissolve 24.4 grams of chrome alum at 25°) and forms a violet solution. If this solution be heated above 60° it turns green, and can then only be made to crystallize with difficulty on standing for a long time. Chrome alum is used as a mordant in dyeing, and for tanning leather.

The corresponding sodium and ammonium chromium alums are also known and used.

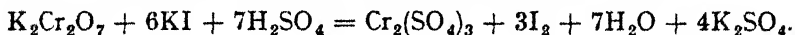
**Perchromates.** Solutions of chromates of the alkali metals yield red salts, of the formula  $M_2CrO_4$  ( $M = Na$  or  $K$ ) when treated with hydrogen peroxide at temperatures below 0°. With dilute acids these salts evolve oxygen and form blue compounds. Compare also page 326.

### § 7 Detection and Determination of Chromium

The presence of chromium is conveniently detected by fusing the compound suspected of containing it with sodium carbonate and a little nitre, when a yellow mass of sodium chromate results if chromium be present. This may be confirmed by dissolving the mass in water, acidifying with acetic acid and adding barium chloride, when a bright yellow precipitate of barium chromate is thrown down.

Chromates are also detected by the formation of a deep blue colour when hydrogen peroxide is added to a solution acidified with sulphuric acid. (Cf. page 326.) The substance causing this blue colour (probably  $CrO_5$ ) dissolves in ether in which it is more stable than in water.

Chromium in the form of chromate or dichromate is determined volumetrically by titrating a standard ferrous sulphate solution. Formerly potassium ferricyanide was used as external indicator, but internal indicators such as *N*-phenyl anthranilic acid or tri-orthophenanthroline ferrous sulphate (*ferroin*) are now often used. Alternatively, a known quantity of chromate or dichromate solution is added to excess of acidified potassium iodide solution; the liberated iodine is then titrated with standard sodium thiosulphate solution:



If the chromium to be determined be present as a chromic salt it may be treated as above, after oxidation by hydrogen peroxide and sodium hydroxide; excess peroxide being removed by boiling.

Chromium is determined gravimetrically by precipitation as chromic hydroxide by adding ammonium chloride and ammonia to the solution of a chromic salt. The hydroxide is filtered off and ignited to the oxide which is weighed. Chromates and dichromates must first be reduced to the chromic state, e.g., with sulphur dioxide.

### § 8 Molybdenum, Mo

#### History and Occurrence

The term *μόλυβδος* (*molybdos*) was applied by the Greeks to galena and other lead ores. Up to the middle of the eighteenth century, the

mineral molybdate or molybdenite was supposed to be identical with graphite, then known as "plumbago" or "black lead." In 1778 K. W. Scheele, in his *Treatise on Molybdena*, showed that, unlike plumbago or graphite, molybdenite forms a "peculiar white earth" when treated with nitric acid. This he proved to have acid properties, and he called it "acidum molybdenae," that is, molybdic acid; and he correctly considered the mineral molybdenite to be a molybdenum sulphide. In 1790 P. J. Hjelm isolated the element as a metallic powder by heating molybdic acid with charcoal.

The principal ore of molybdenum is *molybdenite*,  $\text{MoS}_2$ ; it occurs also as *wulfenite*,  $\text{PbMoO}_4$ , and *molybdate*,  $\text{MoO}_3$ .

### Extraction

The molybdenite is first concentrated mechanically and the concentrate is roasted, whereby it is converted into molybdenum trioxide,  $\text{MoO}_3$ . From this the metal can be obtained by the aluminothermic process, as in the case of chromium (q.v.). It is obtained industrially by reduction with hydrogen. This is usually carried out in two stages on account of the volatility of molybdenum trioxide at  $1000^\circ$  when it sublimes. Reduction to the dioxide is effected at a relatively low temperature; the dioxide is not volatile and so can be reduced to the metal at  $1100^\circ$ .

### Properties

Molybdenum is a fairly hard white metal, which remains unchanged on exposure to air at ordinary temperatures, but is slowly oxidized at a red heat to the trioxide. It has a high melting point,  $2625^\circ$ , and its specific gravity is 10.2. It is only slowly attacked by acids; but hydrochloric acid, nitric acid and hot concentrated sulphuric acid will react with it.

### Uses

Molybdenum is now used industrially to a large extent; in particular, for the manufacture of alloy steels. For this purpose, a ferro-molybdenum alloy is made by reducing molybdenite with iron and carbon in an electric furnace; or by reducing a mixture of molybdenum and iron oxides aluminothermically.

Nickel-molybdenum steel is used for making gun barrels, propeller shafts, etc., and chromium-molybdenum steel tubes have been used in aircraft construction since they can be welded with but little loss of strength. The most important use of molybdenum is in the making of **high-speed tool steels**. These steels, unlike ordinary carbon steels, have the peculiar property of retaining their hardness when heated to a high degree, so that it is possible to make heavy cuts at high speed, for the steel can be heated to dull redness without impairing its quality. Some of the molybdenum and tungsten steels resist the action of acids unusually well, so that these *acid-proof steels* are useful in many chemical

industries. Thus, an alloy containing about 60 per cent of chromium, 35 per cent of iron, and 2-3 per cent of molybdenum is scarcely affected by dilute hydrochloric, nitric, or sulphuric acid, or by boiling aqua regia.

Molybdenum is used for the filament supports of electric lamps, and molybdenum compounds can also be used as a blue pigment in porcelain painting; in silk and woollen dyeing; and in colouring leather and rubber—it has been, indeed, proposed for dyeing fabrics as a substitute for indigo. Ammonium molybdate is largely used in the determination of phosphorus in iron and steel. Molybdenum sulphide is being used for high-temperature lubrication; its action appears to be akin to that of graphite.

Molybdenum forms five oxides, viz.:

Molybdenum sesquioxide,  $\text{Mo}_2\text{O}_3$ ,  
 Molybdenum dioxide,  $\text{MoO}_2$ ,  
 Blue molybdenum oxide,  $\text{Mo}_3\text{O}_8$ ,  
 Molybdenum pentoxide,  $\text{Mo}_5\text{O}_{15}$ ,  
 Molybdenum trioxide,  $\text{MoO}_3$ .

Of these the **blue oxide** and the trioxide are the most interesting. The former is made by allowing powdered molybdenum to remain for a long time in contact with a suspension of the trioxide in water at the ordinary temperature. It is a dark blue substance which forms a blue colloidal solution. It is used as a pigment for rubber, etc

**Molybdenum trioxide**,  $\text{MoO}_3$ , is made by roasting molybdenite. It can be purified by acting upon it with ammonia, which forms a solution of ammonium molybdate, from which copper, if present, is removed by means of ammonium sulphide. The molybdate is then ignited and molybdenum trioxide remains.

It is a white solid which is sparingly soluble in water, forming an acid solution. With alkalis it forms molybdates, but is much less acidic in nature than the corresponding chromium trioxide, and exhibits an even more marked tendency to form complex or condensed acids.

**Molybdic acid**,  $\text{H}_2\text{MoO}_4$ , can be prepared from ammonium molybdate, the commonest salt of this acid, by the action of nitric acid. It forms yellow crusts which give colloidal solutions with water.

### Molybdates

The molybdates do not, as a rule, have simple formulae, such as  $\text{X}_2\text{MoO}_4$ , because of the readiness with which polymolybdates are formed. **Ammonium molybdate**, for instance, is represented by the formula  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{41} \cdot 4\text{H}_2\text{O}$ , i.e., as a derivative of a hepta-molybdic acid. It is made by acting upon molybdenum trioxide with aqueous ammonia, and allowing the solution to crystallize.

Ammonium molybdate is important as a reagent for the detection and determination of phosphates (see page 829). When dissolved in nitric acid and added to a solution of a phosphate, a yellow precipitate of **ammonium phospho-molybdate** is formed. The exact composition of this precipitate varies a little according to the degree of "condensation" or "complexity" of the salt, but is usually  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 6\text{H}_2\text{O}$  or  $(\text{NH}_4)_3\text{Mo}_7\text{PO}_{41} \cdot 6\text{H}_2\text{O}$ . Silicates, arsenates and vanadates give similar complex molybdate derivatives under appropriate conditions.

### Salts of Molybdenum

No salts of molybdenum are known in which the element is definitely present as a basic radical. Chlorides of the following formulae are known, viz.,  $\text{MoCl}_3$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_5$  and  $\text{MoCl}_6$ , but they are not true salts; they either form complexes or are volatile, covalent compounds.



## § 9 Tungsten, W

### History

Tungsten is now an element of great commercial and industrial importance, but until relatively recently it was thought of as rare and unimportant.

Up to the middle of the eighteenth century, the minerals scheelite—formerly called “tungsten” (heavy stone)—and wolframite were supposed to be ores of tin, but, in 1781, K. W. Scheele demonstrated that scheelite contains a peculiar acid, which he called tungstic acid, united with lime as a base. The same year, T. Bergman recognized tungstic acid as an oxide of a new element, tungsten, which was isolated by J. J. y Don Fausto d'Elhuyar in 1783.

### Occurrence

The chief tungsten minerals are *wolframite*, which is a mixture of iron and manganese tungstates,  $(\text{Fe}, \text{Mn})\text{WO}_4$ ; and *scheelite*, calcium tungstate,  $\text{CaWO}_4$ . Other minerals containing tungsten are *stolzite*,  $\text{PbWO}_4$ , *cuproscheelite*,  $\text{CuWO}_4$ , and *tungstenite*,  $\text{WS}_2$ .

### Extraction

Wolframite and scheelite are the principal sources of commercial tungsten. It is a markedly magnetic material, and this property is made use of in a magnetic separator for concentrating the ore. Several methods are in use for obtaining the metal. In one process, the ore is extracted with hydrochloric acid, when a precipitate of tungsten trioxide remains. This is dissolved in ammonia and the tungstate so formed is crystallized and ignited. The separation of molybdenum from tungsten on the technical scale is difficult; for the manufacture of tungsten for electric lamp filaments a molybdenum free ore is used: for the ferro-tungsten used by the steel industry the presence of a little molybdenum is not injurious and so ores containing molybdenum can be used. The trioxide is then reduced by means of hydrogen, or calcium, or by electrolysis in a fused mixture of tungstates. Alternatively, carbon is used as reducing agent when a very pure product is not required. For example, in making ferro-tungsten, for steel manufacture, wolframite is reduced directly in an electric furnace. Another method of obtaining the trioxide from the ore is by heating it with sodium carbonate and extracting the sodium tungstate formed with water; after which calcium tungstate is precipitated by addition of calcium chloride, and decomposed by acidification. A third method consists in mixing the ore with carbon and heating the mixture in a stream of chlorine. Tungsten oxychloride, mixed with chlorides of iron and manganese, is formed; on addition of water tungsten trioxide results.

### Properties

Tungsten is a hard silvery-white metal. It has the highest melting point ( $3380^{\circ}$ ) of any metal, and its specific gravity (19.3) is only exceeded by rhenium, iridium, osmium and platinum and equals that of gold.

Tungsten is too refractory to be melted and cast like other metals and its preparation in ductile forms (as wire and rod) is one of the great achievements of modern metallurgy. The pure powder, obtained by reducing the trioxide with hydrogen at  $1200^{\circ}$ , is compressed into a rod and sintered, in an atmosphere of hydrogen, at  $2500^{\circ}$ . A very heavy electric current is then passed through it which raises its temperature to  $3000^{\circ}$  and converts it into a compact mass. This is then rolled and hammered at  $1500^{\circ}$  after which it can be drawn into wire through diamond or carbide dies at  $400^{\circ}$ – $650^{\circ}$ . Tungsten wire has a high tensile strength and is hard. It is very resistant to chemical action. It is not oxidized below a bright red heat; and chlorine only attacks it at this temperature. Acids are almost without action, but it is readily oxidized by fused potassium chlorate, etc. In chemical properties generally, tungsten resembles molybdenum; but the relationship is less close than between niobium and tantalum.

### Uses

The principal uses of tungsten are for making special steels, and the filaments of electric lamps. Steel containing 14–22 per cent tungsten and 3–5 per cent of chromium constitutes a high-speed tool steel since it retains its hardness even at high temperatures. Tungsten forms some very hard alloys such as *kenna metal* (a tungsten-titanium carbide), *stellite* (an alloy with chromium and cobalt) and *widiametal* (tungsten carbide with 10 per cent of cobalt). Other uses are for anti-cathodes in X-ray tubes and as a sinter with copper and nickel powder as a protection from X-rays and  $\gamma$ -rays.

Some compounds of tungsten also have technical applications. Thus, sodium tungstate is used for "fireproofing" fabrics, and also as a mordant in dyeing. Lead tungstate has been tried as a substitute for white lead, and the trioxide is used as a yellow pigment.

Tungsten forms three oxides, viz.,  $\text{WO}_2$ ,  $\text{W}_2\text{O}_5$  and  $\text{WO}_3$ . **Tungsten dioxide**,  $\text{WO}_2$ , is obtained by reduction of the trioxide by hydrogen. **Blue tungsten oxide**,  $\text{W}_2\text{O}_5$ , somewhat resembles the blue oxide of molybdenum. **Tungsten trioxide**,  $\text{WO}_3$ , is the most important oxide of tungsten. Its preparation from wolframite has been described above. It is a canary-yellow powder, which is insoluble in water, but reacts with alkali hydroxide solutions, forming tungstates.

**Tungstic acid**,  $\text{H}_2\text{WO}_4$ , is obtained when solutions of soluble tungstates, e.g., sodium tungstate, are acidified with hydrochloric acid. From a cold solution,  $\alpha$ -tungstic acid is precipitated and has the formula  $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ . It is slightly soluble in water; but hot solutions, when acidified, give  $\beta$ -tungstic acid,  $\text{H}_2\text{WO}_4$ . Tungstic acid resembles molybdic acid, particularly in its ability to form derivatives of condensed and complex acids. Thus **sodium tungstate** is given formula  $\text{Na}_{10}\text{W}_{12}\text{O}_{41} \cdot 28\text{H}_2\text{O}$ . Phosphates, arsenates, silicates and vanadates form

complex acids and salts with tungstic, as with molybdic acid. Phosphotungstic acid and silicotungstic acid are used in organic chemistry for the detection and determination of alkaloids.

Tungsten does not appear to form any true salts in which the tungsten is basic. It forms a number of halides such as  $WF_6$ ,  $WCl_4$ ,  $WCl_5$  and  $WCl_6$ , but these appear to be covalent compounds.

## § 10 Uranium, U

### History

The mineral pitchblende was formerly supposed to be an ore of zinc, iron, or tungsten, but M. H. Klaproth (1789) proved that it contained what he styled a "half-metallic substance" different from the three elements just named. This element was named "uranium" in honour of Herschel's discovery of the planet Uranus in 1781. E. M. Péligot proved that Klaproth's element was really an oxide of uranium, and he isolated the metal itself in 1842.

### Occurrence

Uranium occurs as *pitchblende* or *uraninite*,  $U_3O_8$ , as *carnotite*,  $KUO_2(VO_4) \cdot 3H_2O$ , and in several other minerals. All uranium minerals are now important as a source of radium and of the uranium isotopes which undergo atomic fission (see below) and which are used for the release of atomic energy. (See Chapter 12.)

### Extraction

Uranium metal is prepared from the dioxide obtained from pitchblende by a complicated series of processes. The dioxide is either converted into the tetrafluoride by heating with hydrofluoric acid and then reduced with metallic calcium or the dioxide is reduced directly with carbon in an electric furnace.

### Properties

Uranium is a white metal in bulk, but as obtained by reduction it is a black powder. Its melting point is  $1132^\circ$  and its specific gravity is 18.7. It is a somewhat reactive metal, being considerably more readily oxidized and attacked by acids than are molybdenum or tungsten. Many of the most interesting properties of uranium are connected with its radioactivity. These are discussed in Chapters 10 and 12.

Uranium is now of very great importance since it is, at present, the only practicable source of atomic energy (*cf.* Chapter 12). By comparison, its other uses are relatively unimportant and employ comparatively small amounts of uranium.

### Uses

Uranium compounds, particularly the yellow trioxide and sodium di-uranate, are used as colours in glass and pottery manufacture. Uranyl nitrate, and acetate, are used for the determination of phosphates, and zinc and magnesium uranyl acetates are reagents for the detection of sodium.

Uranium forms a number of oxides, e.g.,  $UO_2$ ,  $U_2O_4$ ,  $U_3O_8$ ,  $UO_3$  and  $UO_4$ .

**Uranous oxide**,  $UO_2$ , is made from pitchblende for reduction to the element. The concentrated mineral is boiled with nitric acid, other metals precipitated with sodium carbonate and sodium uranate obtained from the solution. This is converted by nitric acid into uranyl nitrate,  $UO_2(NO_3)_2$ , from which the *peroxide*  $UO_4$  is precipitated by ammoniacal hydrogen peroxide. Heating converts this into the **trioxide**,  $UO_3$ , which is reduced to the dioxide by heating in an atmosphere of ammonia and was at one time mistaken for the element. (*Cf.* vanadous oxide, page 855.)

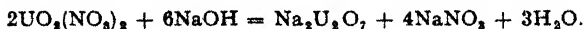
**Urano-uranic oxide**,  $U_3O_8$ , occurs as pitchblende and is made by heating the other oxides in oxygen or by heating uranyl acetate. It is a green powder.

Uranium trioxide,  $\text{UO}_3$ , is a yellow solid made by heating uranyl nitrate in oxygen:



It is an amphoteric oxide, forming uranates with alkalis, and uranyl salts with acids.

The uranates resemble the chromates; salts derived from condensed uranic acids are known, analogous to the polychromates. Sodium di-uranate,  $\text{Na}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$  (also known as *uranium yellow*), is analogous to sodium dichromate. It is made by adding sodium hydroxide to uranium nitrate solution:



### Salts of Uranium

Uranium forms two series of salts, the uranous salts derived from uranous oxide, and the uranic or uranyl salts in which the group  $\text{UO}_2$  acts as a bivalent basic radical. The uranous salts are powerful reducing agents, being readily oxidized to uranyl derivatives. The uranyl salts are characterized by strong fluorescence in solution.

Uranous chloride,  $\text{UCl}_4$ , is obtained as a dark green solid when chlorine is passed over heated uranium.

Uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , commercially known as uranium nitrate, is made by acting upon any of the oxides of uranium with nitric acid. It is a greenish-yellow crystalline solid and is the most important uranium compound. It is readily soluble in water (100 grams of water dissolve 200 grams of the salt at  $18^\circ$ ) and its solutions are used for the volumetric estimation of phosphoric acid, since it forms a yellow precipitate of uranyl ammonium phosphate,  $\text{UO}_2(\text{NH}_4)\text{PO}_4$ , when added to solutions of soluble phosphates. Potassium ferrocyanide is used as external indicator; it gives a brown coloration when excess of uranyl nitrate is present.

Uranyl acetate,  $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , is sometimes used instead of the nitrate as a reagent for phosphates. It is also used for the precipitation of sodium as its double salt with zinc or magnesium acetate (page 635). It is made by dissolving uranium trioxide in acetic acid. It is a yellow crystalline salt, soluble in water (100 grams of water dissolve 7.7 grams of the salt at  $15^\circ$ ).

## § 11 The Relationships of the Group VI Elements

The elements of Group VI fall into two well-defined sections; oxygen, sulphur, selenium, tellurium and polonium comprising one, and the transition elements, chromium, molybdenum, tungsten and uranium, the other. As would be expected of a group in this position in the table, there are marked differences between the two sub-groups, and the resemblances are not very pronounced. But among themselves the elements of each section show resemblances and relationships such as would be anticipated.

All the members of the group, except oxygen, form trioxides with marked acidic properties, and these trioxides give rise to series of isomorphous salts of the type  $\text{M}_2\text{RO}_4$  (where M is a monovalent metal and R is an element of Group VI). The trioxides show a great tendency to form condensed and complex derivatives such as the disulphates, polychromates, etc., a tendency particularly noticeable in the A sub-group. Compounds of the type  $\text{RO}_2\text{Cl}_2$  are also formed by all these

elements, and mostly behave as non-metallic chlorides, being readily hydrolysed by water. With increasing atomic weight, however, the stability increases, and basic character begins to show itself, so that in the case of uranium the basic radical  $\text{UO}_2$  gives rise to the most characteristic and stable of the uranium salts.

Most of the elements in Group VI form dioxides, but whereas those of sulphur and tellurium are feebly acidic, the others are basic. All the elements of the group exhibit variable valency. Oxygen is bivalent as a rule, but occasionally quadrivalent; sulphur, selenium and tellurium exhibit valencies of two, four and six. The A sub-group elements show very variable valencies, but all have a valency of six in their most characteristic oxygen compounds.

As mentioned already, in spite of these similarities, the group falls into two very clearly defined sections; one predominantly metallic in character, the other mainly non-metallic.

The members of the A sub-group, comprising chromium, molybdenum, tungsten and uranium, are all characteristic metals with high melting points (tungsten has the highest melting point of any metal), and the elements are only extracted from their compounds with difficulty. The gradation in their physical properties with atomic weight is indicated by Table LXIII.

TABLE LXIII.—PHYSICAL PROPERTIES OF THE CHROMIUM FAMILY

	Chromium	Molybdenum	Tungsten	Uranium
Atomic weight	52.01	95.95	183.86	238.07
Specific gravity	7.1	10.2	19.3	18.7
Atomic volume	7.7	10.2	9.6	12.7
Melting point	1800°	2625°	3380°	1132°

These metals all combine directly with oxygen, sulphur and nitrogen; and their tendency to form complex acids, which reaches a climax in tungsten, is particularly noteworthy.

The probable electronic configurations of these elements are given in Table LXV. Consideration of this table, along with Table XII (page 150), shows that the metals of this group are *transition elements*, i.e., they occur in that portion of the table where the penultimate electron shell is expanding. Consequently, we should expect to find considerable resemblances between these elements and their horizontal neighbours, e.g., between vanadium, chromium and manganese; and also the development of variable valency and the formation of coloured compounds. All these expectations are, in fact, realized.

The table shows that in each case the last two electron shells have respectively 13 and 1, or 12 and 2 electrons. The 13-group is made up of a complete quantum group of 8 electrons and an incomplete one of 5 electrons. The 12-group (in tungsten) is similarly composed of a complete group of 8, and an incomplete one of 4 electrons. These latter, and

the outermost electrons, can be detached for compound formation; hence the formation of compounds with valencies of 2, 3 and 6.

Turning now to the other section of this group, oxygen, sulphur, selenium, tellurium and polonium are mainly non-metallic in character, although the last three show some signs of metalloid characteristics. All are easily vaporized, have low melting points and can be extracted from their compounds with comparatively little difficulty. Some of the principal properties are summarized in Table LXIV.

TABLE LXIV.—PROPERTIES OF THE OXYGEN-SULPHUR FAMILY

	Oxygen	Sulphur	Selenium	Tellurium
Atomic weight . . .	16	32.066	78.96	127.61
Melting point . . .	-218.8°	112°	220°	452°
Boiling point . . .	-182.97°	444.6°	685°	1007°
Specific gravity (solid) .	1.426	1.96 2.1	4.28-4.80	5.93-6.24
Atomic volume (approx.)	11	16	18	21
Colour of solid . . .	Pale blue	Yellow	Reddish-brown	Black
Heat of union with hydrogen (cals.) .	69.0	4.8	-25.1	-34.9
State of aggregation of hydride . . .	Liquid	Gas	Gas	Gas

These elements all form hydrogen compounds of the same type (the A sub-group metals do not form hydrides), but whereas the hydrogen compounds of sulphur, selenium and tellurium are foetid-smelling gases at ordinary temperatures, water is a colourless, odourless liquid. The acidic character of these hydrides increases with increasing atomic weight, and their stability decreases.

TABLE LXV

Element	Electrons in orbits																
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p	6d	7s
Chromium .	2	2	6	2	6	5	1										
Molybdenum .	2	2	6	2	6	10	2	6	5		1						
Tungsten .	2	2	6	2	6	10	2	6	10	14	2	6	4	2			
Uranium .	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6	5	1

TABLE LXVI

Element	Electrons in orbits										
	1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	5p
Oxygen . . .	2	2	4								
Sulphur . . .	2	2	6	2	4						
Selenium . . .	2	2	6	2	6	10	2	4			
Tellurium . . .	2	2	6	2	6	10	2	6	10	2	4

All four elements (the properties of polonium have scarcely been examined apart from its radioactivity) exhibit allotropy, give rise to characteristic dioxides and (except oxygen) form salts of the type  $M_2RO_3$ , as well as the salts,  $M_2RO_4$ , characteristic of the group as a whole. In this section, the acid  $H_2RO_4$  becomes much less acidic and more unstable as the atomic weight of R increases. Thus telluric acid is a very feeble acid, and decomposes on warming (page 864).

The probable electronic configurations of these elements are given in Table LXVI.

## CHAPTER 38

# THE MANGANESE GROUP

### § 1 Group VII of the Periodic Table

GROUP VII comprises the extremely electronegative halogens, together with, as A sub-group, manganese, technetium and rhenium. The resemblance between these two sub-groups is very slight (see § 8).

### § 2 Manganese, Mn

#### History

Manganese appears to have been used by the ancient Egyptians and Romans for bleaching glass, for their glass often contains the equivalent of up to 2 per cent manganese oxide. Pliny mentions its use for this purpose under the name "magnes"; he considered it to be a variety of loadstone, i.e., a variety of magnetic iron ore. For reasons stated in connection with magnesium, the term "magnesia" in old books may refer to manganese oxide. B. Valentine, and chemists generally towards the end of the eighteenth century, believed wad to be an ore of iron. J. H. Pott (1740) proved that pyrolusite proper does not contain iron, and furnishes a number of salts quite different from those obtained with the iron oxides. C. W. Scheele (1774) made an important investigation on manganese, and T. Bergman (1774) suspected that some metal lay concealed in the mineral earth which he reduced with charcoal, so obtaining a metal regulus. A purer sample was isolated by J. F. John in 1807

#### Occurrence

The metal manganese does not occur free in nature. Much of the manganese ore comes from Russia, and the highest grade picked pyrolusite contains 50 per cent of manganese. Some ore comes from several other countries including India, Africa (South and West) and Brazil. The chief minerals are the oxides *pyrolusite*,  $\text{MnO}_2$ ; *braunite*,  $\text{Mn}_2\text{O}_3$ ; *hausmannite*,  $\text{Mn}_3\text{O}_4$ ; *manganite*,  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . The carbonate,  $\text{MnCO}_3$ , *rhodochrosite* or *rhodochrosite*, is often associated with siderite ( $\text{FeCO}_3$ ); manganese also less frequently occurs as sulphide, *manganese blende*,  $\text{MnS}$ ; and silicate, *rhodonite*,  $\text{MnSiO}_3$ . *Franklinite* (page 714) usually contains manganese as well as iron, and, after the zinc has been extracted, is used in making spiegeleisen. *Wad* is an impure mixture of manganese oxides often found in damp, low-lying places. *Wad* is supposed to be a decomposition product of the manganese minerals.



Minute quantities of manganese occur in water, plants, and animals; and traces also appear to be the colouring agent of many amethyst-coloured minerals.

### Extraction

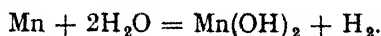
Manganese is largely used in the form of spiegeleisen and ferro-manganese (see below), and this is made by reducing a mixture of oxides of manganese and iron with carbon in a blast furnace.

Manganese itself can be obtained by reduction of any of its oxides with carbon, but an inconveniently high temperature is required and the metal is heavily contaminated with carbon. It is usually obtained by the aluminothermic process, in a similar manner to that described for chromium (page 866). For this purpose, manganese dioxide is first converted into manganosic oxide,  $\text{Mn}_3\text{O}_4$ , by heating it to redness; since the reaction between aluminium and the dioxide is too violent for safety and cannot be directly controlled. Manganese is now being produced on a fairly large scale by the electrolysis of manganous sulphate solution.

The purest metal is made by distilling a sample obtained by the aluminothermic or electrolytic methods.

### Properties

Manganese, when pure, is silvery white but, as usually prepared, it has a yellowish or reddish tinge, like bismuth. It is brittle and intensely hard, as hard as hardened and tempered tool steel. Its specific gravity is 7.4 and it melts at  $1260^\circ$ . It boils at  $2150^\circ$ . Manganese is superficially oxidized when exposed to the air, but the finely divided metal will burn in air. Pure electrolytic manganese is not attacked by water at ordinary temperatures, but steam attacks it slightly. As ordinarily obtained, however, it is readily attacked by water, manganous hydroxide is formed, and hydrogen is evolved:



This behaviour is reminiscent of that of zinc with dilute acids (page 717). When heated in nitrogen, manganese forms the nitride  $\text{Mn}_3\text{N}_2$ ; heated with ammonia it forms a nitride  $\text{Mn}_3\text{N}_2$ . It readily combines with carbon, sulphur and chlorine; and dissolves in acids forming manganous salts with the evolution of hydrogen, even including cold dilute nitric acid.

### Uses

Manganese is used extensively for the manufacture of manganese steel. The annual production of manganese, before the war, was 3,000,000 tons, 80 per cent of which was used for steel-making. All steels contain a little manganese (an average figure being 0.6 per cent), but steel which is required to be tough and to resist wear (e.g., for use for rails) contains up to 1.5 per cent. An alloy containing 12 per cent

of manganese is very hard and tough, and remarkably resistant to shock. It is, therefore, used for rock crushers, railway points and crossings, dredger buckets, steel helmets, etc. Manganese also enters into the composition of several other useful alloys such as *manganese bronze* (copper alloyed with varying quantities of manganese and zinc), *manganin* (83 per cent copper, 13 per cent manganese, 4 per cent nickel). Manganin is used for resistance coils on account of its very small temperature coefficient of resistance.

*Spiegeleisen* and *ferro-manganese* are alloys of manganese, iron and carbon which are used in the Bessemer process (page 907) for reducing iron oxide formed in the converter, and to counteract the deleterious effects of phosphorus and sulphur. Alloys containing less than 20 per cent of iron are called ferro-manganese, the others spiegeleisen.

*Silico-spiegel* is a similar alloy containing up to 10 per cent of silicon in addition.

*Cupro-manganese* and *Heusler's alloy* (55 per cent copper, 15 per cent aluminium and 30 per cent manganese) are magnetic.

Manganese dioxide is used as an oxidizing agent. It is used in decolorizing glass stained by the traces of "ferric silicate" present, for the violet colour of manganese silicate masks the complementary green tint of the iron. Manganese borate and some organic salts of manganese are also used as "driers" for paints and varnishes; manganese dioxide as a depolarizer in battery cells; and for colouring pottery bodies and glazes. Wad is used in the manufacture of paint. A crude mixture of sodium manganate and permanganate is made by fusing sodium hydroxide with pyrolusite, and a solution of the product is sold as a disinfectant under the name "Condy's fluid."

### Atomic Weight

The atomic weight of manganese is seen to be in the neighbourhood of 55 from the value of its specific heat (0.114). The exact value has been estimated by analyses of silver permanganate, and by conversion of manganous chloride and bromide into the corresponding silver halides and by accurate determination of the mass number by physical methods. The value recommended at present (1957) by the International Committee is 54.94.

### § 3 Oxides of Manganese

Manganese forms an unusually large number of definite oxides, viz.:

Manganous oxide,  $\text{MnO}$ ,  
Manganosic oxide,  $\text{Mn}_3\text{O}_4$ ,  
Manganese sesquioxide,  $\text{Mn}_2\text{O}_3$ ,  
Manganese dioxide,  $\text{MnO}_2$ ,  
Manganese trioxide,  $\text{MnO}_3$ ,  
Manganese heptoxide,  $\text{Mn}_2\text{O}_7$ .

**Manganous Oxide, MnO**

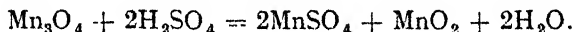
This oxide can be obtained by reducing any of the other oxides by heating in a steam of hydrogen, and also by heating manganous hydroxide or carbonate in absence of air. It is also formed by heating manganous oxalate.

It is a greenish powder which oxidizes rapidly on exposure to air. It reacts with acids, forming manganous salts.

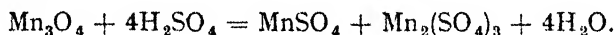
**Manganous hydroxide**,  $\text{Mn}(\text{OH})_2$ , is prepared by adding an alkali hydroxide to a solution of a manganous salt, in absence of air, when it is precipitated as a white, flocculent precipitate. In the air, it is quickly oxidized, probably to manganic hydroxide. It is slightly soluble in water, and forms manganous salts with acids.

**Manganosic Oxide, Trimanganese Tetroxide,  $\text{Mn}_3\text{O}_4$** 

This oxide, also called red oxide of manganese, occurs in nature in red, prismatic crystals of *hausmanite*; and it is formed as a brownish-red powder when any other manganese oxide is ignited in air. It can be obtained, in a crystalline condition, by heating the powdered oxide in a slow current of hydrogen chloride. Manganosic oxide reacts with acids with the formation of a soluble manganous salt and insoluble hydrated manganese dioxide, e.g., when heated with dilute sulphuric acid:



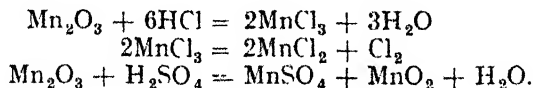
Dilute nitric acid acts upon it similarly. On the other hand, cold concentrated sulphuric acid gives a mixture of manganous and manganic sulphates:



It thus appears to be a compound oxide, analogous to red lead (page 795) and the black oxide of iron (page 918).

**Manganese Sesquioxide,  $\text{Mn}_2\text{O}_3$** 

This oxide occurs in nature as *braunite*,  $3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$ . It is obtained as a black powder when any other oxide of manganese is heated to about  $900^\circ$  in a current of oxygen. Manganese sesquioxide reacts slowly with cold, dilute acids, forming manganic salts; hot sulphuric acid forms manganous sulphate and manganese dioxide; when warmed with hydrochloric acid, manganous chloride and chlorine result:



The corresponding hydroxide,  $\text{Mn}(\text{OH})_3$ , has not been isolated, but

the hydroxide  $\text{MnO} \cdot \text{OH}$  (or  $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) is obtained by the action of chlorine on a suspension of manganous carbonate in water:

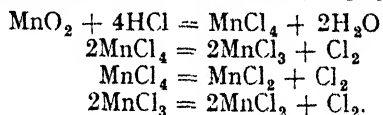


This hydroxide also occurs native as the mineral *manganite*.

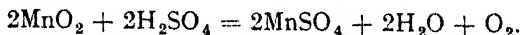
### Manganese Dioxide, $\text{MnO}_2$

This is the most important compound of manganese. It occurs native as *pyrolusite*, *psilomelane*, a hydrated form, and *wad*, a less pure form, contaminated with earthy material. Commercial manganese dioxide is prepared from pyrolusite.

Manganese dioxide, which is difficult to obtain pure, is a black insoluble powder. On heating to redness it is converted, with loss of oxygen, into manganous oxide. It is not affected by dilute acids, except hydrochloric acid. Cold concentrated hydrochloric acid dissolves it, giving a dark brown liquid and very little chlorine, if the temperature be kept low. This solution may possibly contain manganese tetrachloride, but probably consists of the trichloride. On warming, chlorine is evolved and manganous chloride remains (see page 530).



When heated with concentrated sulphuric acid, manganous sulphate and oxygen are formed. In the cold, it is possible that a disulphate,  $\text{Mn}(\text{SO}_4)_2$ , is formed:



Manganese dioxide appears to be a feebly acidic oxide, for with alkalis it forms compounds which are thought to be manganites (see below). It may also be a very feeble basic oxide; there is no direct evidence of the existence of the tetrachloride in solution, although complex derivatives, such as  $\text{K}_2\text{MnCl}_6$ , are known. It is not a true peroxide or superoxide, since it does not give hydrogen peroxide with acids. It is, therefore, a polyoxide (page 339).

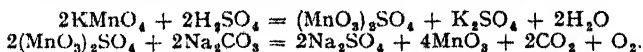
Manganese dioxide is used in the preparation of chlorine (page 530); for neutralization of the green colour of glass; in the manufacture of Leclanché cells (both of the wet and dry types) as a depolarizer; and for the manufacture of permanganates and other manganese compounds in chemical industry.

*Hydrated manganese dioxide* is obtained when manganese dioxide is precipitated from a reaction in solution. It is probably manganous acid (q.v., page 891).

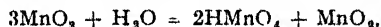
### Manganese Trioxide, $\text{MnO}_3$

If solid potassium permanganate be dissolved in cold concentrated sulphuric acid, and the green solution (probably containing permanganyl-sulphate) dropped

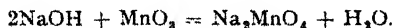
upon anhydrous sodium carbonate, violet fumes are evolved which may be condensed to a red, viscid solid, believed to be manganese trioxide:



It reacts with water forming manganese dioxide and permanganic acid:



and with alkali hydroxides, it gives manganates, e.g.:



It is not finally established that the red solid is manganese trioxide; it has been thought by some to be a mixture of the heptoxide (q.v.) with a lower oxide.

#### Manganese Heptoxide, $\text{Mn}_2\text{O}_7$ ,

If the green solution obtained by dissolving potassium permanganate in cold concentrated sulphuric acid be treated with a little ice-cold water, only drops of manganese heptoxide separate. It is a reddish-brown liquid which does not solidify at  $-20^\circ$ . It is very unstable, and decomposes explosively on warming into manganese dioxide and oxygen. It dissolves in water, forming a violet solution of permanganic acid. It is thus permanganic anhydride. It is a very powerful oxidizing agent, causing wood to inflame when brought into contact with it, and mixed with sulphur or phosphorus, the mixture is violently explosive.

### § 4 Oxyacids of Manganese

Salts are known derived from three oxyacids of manganese, viz.:

Manganites from manganous acid,  $\text{H}_2\text{MnO}_3$ ,

Manganates from manganic acid,  $\text{H}_2\text{MnO}_4$ ,

Permanganates from permanganic acid,  $\text{HMnO}_4$ ,

of which manganic acid itself has not been isolated.

#### Manganous Acid, $\text{H}_2\text{MnO}_3$

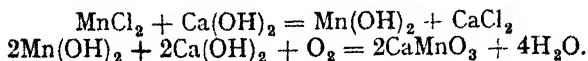
When manganese dioxide is precipitated as the result of reactions in solution, it is usually obtained in a hydrated form, which may be manganous acid— $\text{MnO}_2 \cdot \text{H}_2\text{O}$  or  $\text{H}_2\text{MnO}_3$ . It is conveniently made thus by addition of an alkaline hypochlorite solution to an aqueous solution of a manganous salt.



Manganese dioxide, particularly in this form, reacts with alkali hydroxide solutions to form manganites. Also, when manganese dioxide is fused with potassium hydroxide in absence of air, **potassium manganite**,  $\text{K}_2\text{MnO}_3$ , is believed to be formed. **Calcium manganite**,  $\text{CaMnO}_3$ , was probably the chief constituent of the *manganese mud* obtained in the (now obsolete) Weldon recovery process for chlorine.

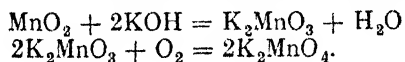
In this process pyrolusite was used to oxidize hydrochloric acid. The hot residual liquor, after the chlorine had been evolved, consisted mainly of manganous chloride; this was treated with excess of milk of lime and

air was blown through the mixture for some hours. When allowed to settle out the *manganese mud* or *Weldon mud* separated and was used for the oxidation of a further quantity of hydrochloric acid. The equations for the reactions involved have been said to be:



### Manganates

Manganic acid has not so far been isolated, but various manganates are known. When manganese dioxide is fused with potassium or sodium hydroxide, in presence of air or an oxidizing agent such as potassium nitrate or chlorate, the potassium or sodium manganite first formed is converted into the corresponding manganate:



The fused mass so obtained has a dark green colour, and when extracted with a small quantity of water it furnishes a dark green solution from which dark green crystals of **potassium manganate**,  $\text{K}_2\text{MnO}_4$ , can be obtained by allowing the solution to evaporate, at ordinary temperatures, *in vacuo*. **Sodium manganate**,  $\text{Na}_2\text{MnO}_4 \cdot 10\text{H}_2\text{O}$ , can be made similarly, and also by fusing manganese dioxide with sodium peroxide. It is isomorphous with Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ .

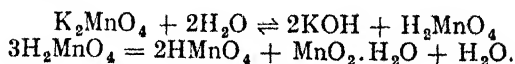
The manganates are strong oxidizing agents, but they are so readily converted into the corresponding permanganates (see below), and these are so much more convenient, that manganates are not generally used.

### Permanganic Acid, $\text{HMnO}_4$

This acid is best made by adding just sufficient sulphuric acid to barium permanganate (see below) to precipitate the barium as sulphate. On evaporating the filtered solution, violet crystals of permanganic acid are obtained. It is a powerful oxidizing agent like perchloric acid, which it resembles also in decomposing in contact with organic matter.

### Potassium Permanganate, $\text{KMnO}_4$

When the green concentrated solution of potassium manganate, prepared as described above, is gently warmed, or largely diluted with water, the green colour changes to pink owing to the formation of potassium permanganate, and hydrated manganese dioxide is precipitated. It is supposed that the manganate is first hydrolysed, forming manganic acid, which is so unstable that it is at once converted into permanganic acid:

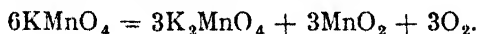


The manganate is thus self-oxidized and self-reduced; one part of the compound being oxidized at the expense of the oxygen in another part. Potassium manganate is not hydrolysed in alkaline solutions, and it is supposed that pure water will not hydrolyse it. If a small trace of acid be present, even carbonic acid derived from the atmosphere, hydrolysis takes place. Hence, if carbon dioxide be passed through potassium manganate solution, it is converted into the permanganate:

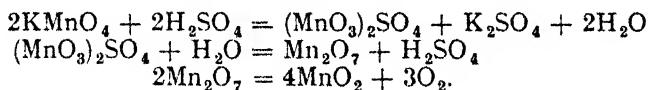


This is the method employed commercially; the solution is run off from the manganese dioxide deposited, and then evaporated until it begins to crystallize.

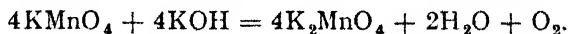
Potassium permanganate forms dark purple, almost black, crystals, with a greenish lustre, which are isomorphous with potassium perchlorate. It is only sparingly soluble in water: 100 grams of water dissolve 4.4 grams at 10°, 5.2 grams at 15° and 6.38 grams at 20°. When heated to about 240°, potassium permanganate decomposes, furnishing oxygen and potassium manganate:



It dissolves in cold concentrated sulphuric acid, forming a green solution of **permanganyl sulphate**,  $(\text{MnO}_3)_2\text{SO}_4$ , which is liable to decompose explosively. A similar explosive decomposition occurs if potassium permanganate be warmed with sulphuric acid, and is probably due to the formation of manganese heptoxide:



Potassium permanganate is a powerful oxidizing agent, and is extensively employed as such in volumetric analysis. When heated with an alkali, potassium permanganate reverts to the manganate:



If a reducing agent be also present, the alkaline permanganate solution is further reduced to manganese dioxide:



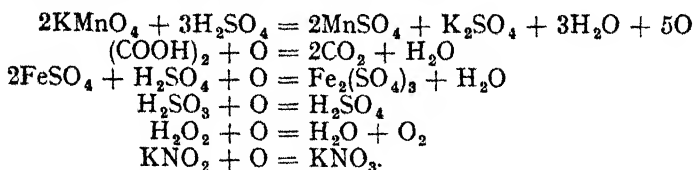
In acid solutions, the reduction proceeds still further, and a manganous salt is formed:



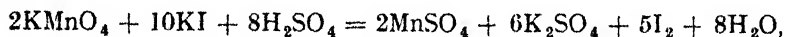
There are thus three stages in the reduction of potassium permanganate corresponding with separation of one, three or five atoms of available oxygen per two molecules of salt.

For volumetric analysis reduction is always carried out in acid

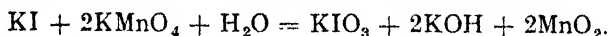
solution (except for the determination of formic acid or formates), and in this way oxalic acid and oxalates, ferrous sulphate, sulphurous acid and sulphites, hydrogen peroxide, nitrous acid and nitrites are determined. In these circumstances two molecules of potassium permanganate yield five atoms of available oxygen:



In acid solution potassium permanganate liberates iodine from potassium iodide solution, a process also employed in volumetric analysis:



but in alkaline solution it is oxidized to potassium iodate:



The use of acid permanganate is very convenient since the solution of the manganous salt formed is colourless, and so, if a solution of potassium permanganate be added to a solution of a reducing agent, a colourless solution results until all the latter has been oxidized when the appearance of a persistent pink colour indicates the end of the reaction.

**Sodium permanganate**,  $\text{NaMnO}_4$ , can be made in a similar way to the potassium salt, but it only crystallizes with difficulty. Consequently it is not much used except in the form of *Condy's fluid*, which is a solution of the crude mixture of sodium manganate and permanganate, made by fusing sodium hydroxide and pyrolusite.

**Silver permanganate**,  $\text{AgMnO}_4$ , separates as a red precipitate when equivalent quantities of hot concentrated solutions of silver nitrate and potassium permanganate are mixed and allowed to cool.

**Barium permanganate**,  $\text{Ba}(\text{MnO}_4)_2$ , is formed on adding barium chloride solution to a solution of silver permanganate. It is used for the preparation of permanganic acid.

## § 5 Salts of Manganese

Manganese forms two series of salts, which are derived respectively from manganous oxide and manganese sesquioxide. They are known as the manganous and manganic salts, of which the latter are unstable.

**Manganous carbonate**,  $\text{MnCO}_3$ , is made by adding sodium carbonate solution to a solution of a manganous salt, when it is precipitated as a pinkish or buff-coloured powder. It decomposes on heating, the manganous oxide first formed being oxidized to manganese dioxide, if access of air be allowed.



**Manganous Chloride,  $\text{MnCl}_2$** 

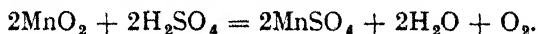
This salt is prepared by dissolving the oxide, or carbonate, in hydrochloric acid and evaporating the solution. It can also be made from pure manganese dioxide similarly, the heating being continued long enough to drive off all free chlorine. It separates from these solutions in rose-pink crystals of the composition  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . The anhydrous salt is made by heating these crystals in a stream of hydrogen chloride. It is a very deliquescent substance and forms complex salts of the type  $\text{R}_2\text{MnCl}_4$  with the alkali metal chlorides.

**Manganous nitrate**,  $\text{Mn}(\text{NO}_3)_2$ , is made by dissolving manganous carbonate in dilute nitric acid. On heating, manganese dioxide is left:



**Manganous sulphide**,  $\text{MnS}$ , is formed as a flesh-coloured precipitate when hydrogen sulphide is passed into an alkaline solution of a manganous salt. It dissolves readily in dilute acids, including acetic acid, which enables it to be distinguished from zinc sulphide which is insoluble in acetic acid.

**Manganous sulphate**,  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , is made commercially by heating pyrolusite with concentrated sulphuric acid:



It is recrystallized from water, and so obtained in pink triclinic crystals of the composition  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ . Some other hydrates are known including a pentahydrate which is isomorphous with copper sulphate.

**Manganous dithionate**,  $\text{MnS}_2\text{O}_8$ , is referred to on page 515.

**Manganous ammonium phosphate**,  $\text{MnNH}_4\text{PO}_4$ , is formed in pink glittering crystals when ammonium chloride, ammonia and sodium phosphate are added to a solution of a manganous salt. It is of importance for the determination of manganese on account of its insolubility and since, on ignition, it is converted into the corresponding pyrophosphate,  $\text{Mn}_2\text{P}_2\text{O}_7$ .

**Manganic salts** are unstable and cannot readily be obtained pure. The brown solution which results when manganese dioxide is added to cold concentrated hydrochloric acid (page 890) probably contains a large proportion of **manganic chloride**,  $\text{MnCl}_3$ . Also, by suspending manganese dioxide in carbon tetrachloride and passing in dry hydrogen chloride, a solid containing manganic chloride results. It is decomposed by water. It forms complex salts such as  $(\text{NH}_4)_2\text{MnCl}_5 \cdot \text{H}_2\text{O}$ , and  $\text{K}_2\text{MnCl}_6 \cdot \text{H}_2\text{O}$ .

**Manganic sulphate**,  $\text{Mn}_2(\text{SO}_4)_3$ , is formed as a dark green powder by the action of sulphuric acid on freshly precipitated manganese dioxide. It dissolves in water to a violet solution which deposits hydrated manganese dioxide on standing. It forms alums such as  $\text{KMn}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

### § 6 Detection and Determination of Manganese

Manganese is often detected by the formation of a green manganate when the substance to be tested is fused with caustic alkali and an oxidizing agent (page 892). On solution in water, a green solution is formed which becomes pink on the addition of dilute sulphuric acid.

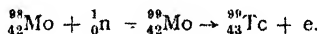
Manganese is determined gravimetrically either by precipitation as the double phosphate with ammonia, which on ignition is converted into the pyrophosphate  $Mn_2P_2O_7$ , or as the sulphide,  $MnS$ .

A convenient method for the determination of manganese in iron or steel depends upon the ability of sodium bismuthate to oxidize manganese compounds in solution to permanganates. The solution of the steel in nitric acid is treated with sodium bismuthate. To the resulting permanganate, after filtration, excess of a standard solution of a ferrous salt is added and the excess of ferrous iron determined by titration with standard permanganate solution.

### § 7 Technetium and Rhenium

When Mendeléeff compiled the first periodic table he left two vacant places in Group VIIA below manganese, which for long has been the only known representative of this sub-group.

Moseley's work (page 136) confirmed the reality of these gaps corresponding to atomic numbers 43 and 75. In 1925 Noddack and Tacke reported the existence of these elements on examining the X-ray spectra of concentrates from certain platinum ores and columbite. One of these elements (43) they called **masurium**, Ma, from Masuren, a district in East Prussia, and the other **rhenium**, Re, after the Rhine. It has since been shown that the element of atomic number 43 does not exist in nature but that it can be obtained, in the form of unstable isotopes, by artificial nuclear reactions such as the bombardment of molybdenum with neutrons in a reactor.



This element is now known as **technetium**, Tc, the name being derived from the Greek *τέχνη* (*technē*) meaning an art or craft, since it was the first new element to be prepared artificially. Several isotopes are known, that of mass number 99 has the longest half-life period ( $2 \times 10^5$  years), all the isotopes known are unstable and radioactive. Recently technetium has been produced pure in quantities of a few grams from the fission products of the fuel elements of nuclear reactors. Little is known as yet about the chemistry of technetium.

Rhenium is a scarce element. It occurs in traces in molybdenite (page 877), columbite (page 856) and pyrolusite. Recently the production of the metal on a commercial scale has been begun in the U.S.A. It is recovered as a by-product of the roasting of molybdenum sulphide and is isolated as ammonium perrhenate. The metal is obtained by reducing this with hydrogen. It is a silver coloured metal of high specific gravity (approx. 20.0) and melting point (3167°). The most important use of rhenium is in thermo-couples, along with tungsten, for the measurement of high temperatures up to 2500°. It forms a number of oxides, some of which are analogous to those of manganese, and perrhenates, corresponding to permanganates, are the principal compounds of rhenium. They are much less powerful oxidizing agents than the permanganates, and are colourless.

### § 8 Relationships of the Elements of Group VIIA

Until comparatively recently, manganese was the only known member of this sub-group, and even now so little is known of the chemistry of technetium that comparisons involving it cannot usefully be made.

So far as the chemistry of rhenium has been investigated there seems to be the sort of resemblance to that of manganese which would be expected in view of their positions in the periodic system. Both elements exhibit very variable valency; both form a large number of oxides, those with the larger proportions of oxygen being acidic in nature and readily forming salts such as the permanganates and perhenates.

Since this is one of the extreme groups of the periodic system, it would be expected that the resemblance between the two sub-groups would be rather slight, as is found, for example, in the case of Group I, where the relationship between the alkali metals and the coinage metals is not at all obvious. In point of fact, the resemblance of manganese and rhenium to the halogens is even slighter, and it can hardly be doubted that but for the indication of Mendeléeff's table no such relationship would have been sought for or upheld.

The only property in which manganese shows any real analogy with the halogens is the formation of a heptoxide,  $Mn_2O_7$ , which gives rise to the permanganates, which are in many respects similar to the perchlorates. Thus, the acids are monobasic and are powerful oxidizing agents, and the corresponding salts are often isomorphous. But the force of this fact is somewhat weakened by the isomorphism of the manganates with the sulphates.

In point of fact, the principal analogies in the chemistry of manganese are with its horizontal neighbours in the periodic system, viz., chromium and iron, as might be anticipated from its being a transitional element (in the modern sense). As examples of these resemblances there may be mentioned the isomorphism of the manganites and chromites; the manganic and ferric alums, and the similarity in the properties of the metals themselves. In all probability, when their chemistry has been more fully investigated, similar relationships will be discerned between molybdenum, technetium and ruthenium; and between tungsten, rhenium and osmium.

The probable electronic configuration of manganese, technetium and rhenium are given in Table LXVII.

TABLE LXVII

Element	Electrons in orbits																
	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	6s	6p	6d	7s
Manganese .	2	2	6	2	6	5	2										
Technetium .	2	2	6	2	6	10	2	6	6		1						
Rhenium .	2	2	6	2	6	10	2	6	10	14	2	6	5	2			

## CHAPTER 39

# IRON, COBALT, NICKEL AND THE PLATINUM METALS

Steel is the mainspring of modern industry. The commercial importance of steel is greater than that of gold, silver, zinc, copper and lead combined, and, indeed, the trite saying that this is an age of iron is well founded.—W. M. JOHNSON (1914).

The progress which has been made and the considerable exactness actually attained in chemical analysis have been owing in a great measure to the discovery of platina. Without the resources placed at the ready disposal of chemists by this invaluable metal, it is difficult to conceive that the multitude of delicate analytical experiments which have been required to construct the fabric of existing knowledge could have ever been performed.—J. F. W. HERSCHEL.

### § 1 Group VIII of the Periodic Table

GROUP VIII of the Periodic Table comprises those elements which Mendeléeff termed transition elements (a name which now has a different and more fundamental significance (page 152)). It differs from all the other groups in containing three sets of three elements, each triad being composed of very similar elements whose atomic numbers differ only by one unit each. They are, in fact, situated more or less in the middle of each run of transition elements (in the modern sense, page 124).

The elements concerned are iron, cobalt and nickel; ruthenium, rhodium and palladium; and osmium, iridium and platinum. The six last named are frequently referred to as a whole as the "platinum metals."

### § 2 Iron, Fe. History and Occurrence

#### History

Iron is perhaps the most precious of all the metals, for civilized man would probably feel its absence more than would be the case if he were deprived of all the so-called precious metals. Early in the fourteenth century, when iron was scarce, some iron kitchen utensils in the household of Edward III are said to have been classed among the jewels; and iron implements were among the most prized objects of plundering freebooters. The name iron is derived from the Scandinavian *iarn*. Several fabulous stories have been told describing how meteoric iron falling to the earth was sent from heaven as a gift of the gods to man and the use of meteoric iron by primitive peoples may well have preceded the knowledge of the art of extracting it from its ores. It has been suggested that "the first iron produced was the result

of chance when lumps of iron ore, in place of stones, formed a rude cooking fire associated with some feast, where the fire was maintained long enough to effect the reduction." Then followed the observation that the higher temperatures obtained when the wind was blowing produced better material. Hence followed various contrivances for producing an artificial blast of wind, and so on by natural stages to the blast furnace. Iron implements have been used from prehistoric times, one was found during some blasting operations in the pyramid at Gizeh (Egypt), which is probably 5000 years old. The use of steel in China has been traced as far back as 2550 B.C., and we are told by the philologists that the early Vedic poets mention iron as being in the possession of their prehistoric ancestors, and that the artisans had acquired considerable skill in fashioning iron into tools. Owing to the fact that ancient objects of iron are comparatively rare, while ancient bronze objects are quite abundant, archaeologists affirm that the so-called *bronze age* preceded the *age of iron*. The argument is much weakened when it is remembered how much more readily iron is corroded by oxidation, and how much more readily bronze would survive atmospheric action. Still, bronze was more easy to extract and work than iron, and archaeologists consider that bronze ceased to be the dominant tool and weapon of civilized peoples about 500 B.C. The scarcity of copper and the abundance of iron in India makes it probable that with the Hindoos the iron age was not preceded by a bronze age. The Aryan emigrants who travelled into Europe carried with them a knowledge of producing iron from its ores. The Etruscans of North Italy were of Aryan stock, and they acquired considerable skill in the working of iron. Soon after the downfall of the Roman Empire, the manufacture of iron developed in Spain. The famous Toledo steel blades were the product of Spanish artisans. Their fame spread, and Spanish craftsmen were drawn into France and Germany and there they introduced their peculiar Catalan forge which subsequently evolved into the large iron-smelting furnaces. The product of the Catalan forge is either a malleable iron or steel; the larger furnaces produced a variety of iron which, being a form of cast iron, could neither be forged nor tempered, although it was very suitable for all kinds of castings of moderate strength. The discovery of a process by Cort—*vide infra*—whereby cast iron could be converted into wrought iron at a far less cost than was possible in the Catalan forge, gave a great impetus to the manufacture of iron in England.

Iron is frequently mentioned in the sacred writings. The Chalybes—an ancient nation living near the Black Sea—are supposed by the Greeks to have been the first to smelt iron ores. Hence the old term *chalybs* for steel, and our modern *chalybeate* for ferruginous. The process of smelting iron was early practised in the East, and the Hindoos acquired considerable skill in the manufacture of wrought iron and steel. The old sword blades of Toledo, Bilbao, and Damascus were very famous. The more recent method of smelting by means of

the blast furnace is said to have been devised in Germany about 1350; and in Great Britain about 1500. Charcoal was first used as the reducing agent; in 1618 D. Dudley commenced using coal; and in 1713 Darby used coke. Coke and coal gradually displaced the use of charcoal. Some charcoal is still used where wood is cheap, e.g., in a few places on the Continent and in America and in Mysore in India.

### Occurrence

Small quantities of metallic iron occur in some basaltic rocks. An unusual mass, over twenty-five tons, has been found on the Disko Island, Greenland. Since iron rapidly corrodes when exposed to a humid atmosphere, native iron is not at all common. Nearly all *meteorites* or *aerolites* contain iron associated with other metals—chiefly copper, cobalt, and nickel. Traces of iron combined in various ways are found scattered almost universally throughout the mineral kingdom. Ferric oxide,  $\text{Fe}_2\text{O}_3$ , is widely distributed in nature as *red haematite*—from the Greek *αἷμα* (*haima*), blood, in reference to the colour of its streak—*red ore*, and *specular iron ore*—from the Latin *speculum*, a mirror, in allusion to the lustrous crystals of this mineral. *Brown haematite* represents a class of hydrated oxides which may be represented by the general formula:  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ , where  $n$  represents the variable amount of water in different varieties—*limonite* is generally taken to be  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , that is,  $\text{Fe}(\text{OH})_3$ ; *göthite*,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; and *bog iron ore* which occurs in Ireland belongs to this class. Limonite and scanthosiderite are considered to be colloidal forms of göthite with various quantities of adsorbed water. *Magnetite*,  $\text{Fe}_3\text{O}_4$ , is called *loadstone*, and *magnetic oxide of iron*. *Siderite*, or *spathic iron ore*,  $\text{FeCO}_3$ , is a ferrous carbonate. *Iron pyrites*,  $\text{FeS}_2$ , and *chalcopyrites* or *cupriferous pyrites*,  $\text{CuFeS}_2$ , are not worked directly for iron on account of the difficulty involved in eliminating sulphur from the product so that iron pyrites is often regarded as a sulphur ore. Very few clays, soils and granite rocks are free from small quantities of iron. Iron plays an important part in the nutrition of higher animals and plants since this element seems necessary for their healthy growth; it is a constituent of the haemoglobin of the blood.

### § 3 The Extraction of Iron from its Ores

The principal sources of commercial iron are the oxides—magnetite and haematite—and carbonates. These ores frequently contain a certain amount of clay and are then termed *clay ironstones*. The so-called *blackband ironstone* is a ferrous carbonate contaminated with clay and black coaly matters. The ores are usually calcined or roasted to drive off most of the moisture and carbon dioxide; to burn the organic matter and some of the sulphur and arsenic; and to convert ferrous oxide to ferric oxide.

This prevents the early formation of a fusible slag which would

attack the lining of the furnace. Ferric oxide does not form a slag at so low a temperature as ferrous oxide. At the same time the ore is made somewhat porous, and this facilitates its reduction to metallic iron at a later stage of the process.

The reduction of the calcined ore or of ferric oxide is effected in a blast furnace.

### The Blast Furnace

The blast furnace is a tall cylindrical furnace—80 to 120 feet high—and shaped approximately as indicated in the section, Fig. 39.1.

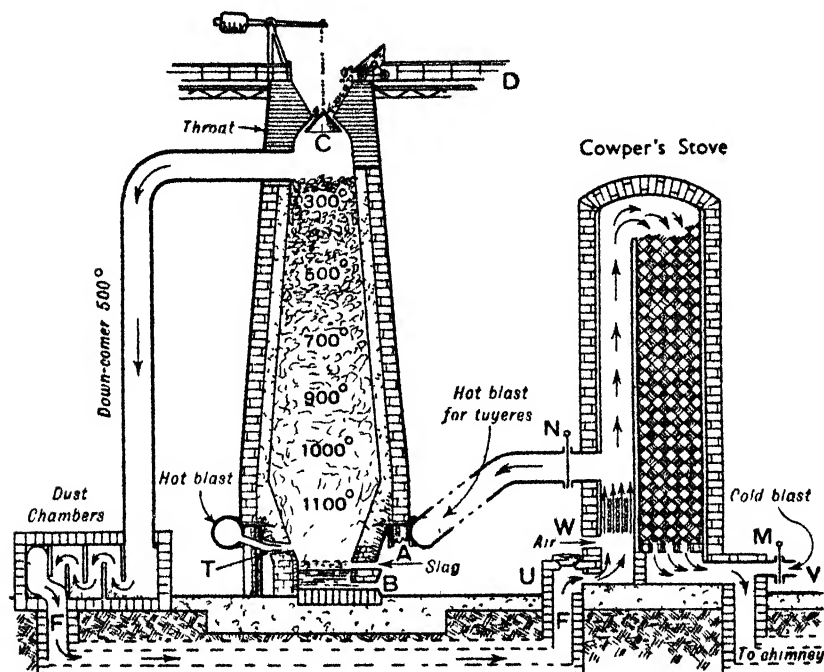


FIG 39.1 —Blast Furnace (Diagrammatic)

The dimensions and constructional details of blast furnaces vary somewhat in different localities. It has an outer shell made of iron plates riveted together. Inside this is a casing of ordinary brickwork, and inside this a lining of firebricks— $1\frac{1}{2}$  feet thick. The parts which are subjected to the greatest heat are built independently so as to facilitate repairs. The greatest internal width is 20 feet. This part is called the *bosh*. The mouth of the furnace is closed by a *cup-and-cone feeder*, C. The materials for charging the furnace are conveyed

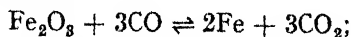
in trucks to the *charging gallery*, *D*, at the top of the furnace, and there tipped into the cup of the feeder. When the cup is filled, the cone is depressed, and the charge automatically distributed in the interior of the furnace. The waste gases pass away via the outlet at the throat of the furnace. The furnace narrows below the boshes, and at the hearth the diameter is 8 feet. Molten iron and slag collect on the hearth, and outlets are here provided, one, *A*, for tapping the slag and another, *B*, for tapping the iron. Between six and eight feet from the base of the furnace, six openings, *T*, are provided for the insertion of water-cooled nozzles—*tuyeres*—through which a blast of hot air is forced into the furnace.

The hot gases from the top of the furnace are led down a flue—the *down-comer*—into a chamber—the *dust-catcher*. The gases pass from the dust-catcher along an underground flue, *FF*, to a tower—*Cowper's stove*—packed checkerwise with firebricks. The flue gas is burnt in the combustion chamber of the stove, and the products of combustion pass on to the chimney. The secondary air required for the combustion of this gas enters through the ports, *W*. The burning gas raises the temperature of the checker brickwork. When the temperature of the stove is hot enough, the gases from the blast furnace are deflected, and burnt in an adjoining similar tower; meanwhile the gas and air valves—*U*, *V*, *W*—in the hot tower are closed; and another set of valves—*M*, *N*—connecting the tuyeres with the blowing machine are opened. The cold air passing through the hot checkerwork of the Cowper's stove on its way to the tuyeres is heated. When the tower has been cooled sufficiently, the adjoining stove is hot. The gas from the blast furnace is again burned in the cooled tower, and the blast is sent through the hot tower.

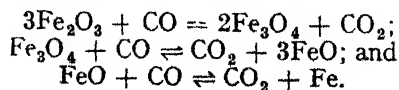
The chemical changes which take place in the blast furnace during the smelting of iron ore are somewhat complex. Hence the following sketch must be regarded as a simplified description:

### 1. The Ore

The ore, mixed with coke and limestone, is exposed, in the upper part of the furnace, to the action of reducing gases, principally carbon monoxide, ascending from the lower part of the furnace. The action commences between 200° and 500°, that is, as soon as the charge has commenced its downward descent:



and reduction continues with increasing velocity as the charge descends into the hotter part of the furnace. There appears to be a complex series of side and intermediate reactions:

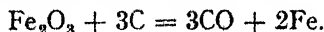




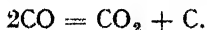
Below dull redness, the back-reaction



is known to occur. Most of the oxide is reduced before it has descended ten feet below the level of the charge; any oxide which has escaped reduction will then be reduced by the carbon:



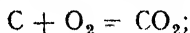
The hot spongy iron meets the ascending carbon monoxide, and decomposes part:



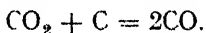
The solid carbon is deposited amidst the spongy iron. The iron undergoes little change until it reaches the zone of fusion. The iron, however, absorbs or dissolves much carbon as it passes down the furnace. The melting point of a mixture of iron and carbon is lower than that of pure iron, so that while the temperature of the blast furnace would not be sufficient to melt pure iron to the necessary fluid condition, the temperature required for iron with carbon in solution is easily maintained. The molten iron trickles down and collects in the well of the furnace below the tuyeres. The iron takes up many other elements in addition to carbon during its descent to the furnace. Thus, silicon, sulphur, phosphorus, and manganese are partly absorbed by the iron, and partly by the slag.

## 2. The Ascending Gases

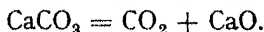
The oxygen of the hot air blast burns the carbon of the hot coke:



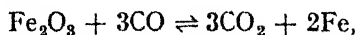
and the carbon dioxide is at once reduced by the hot carbon:



The ascending gases warm up the descending charge. When the temperature reaches about 600°, the limestone begins to decompose:



Most of the carbon dioxide thus formed is at once reduced by the excess of carbon to carbon monoxide. At this stage, the reduction of the iron oxide to spongy metallic iron is practically complete. An excess of carbon monoxide is needed for the reduction because the reaction,



is reversible, and a condition of equilibrium would be attained when only a certain proportion of the ferric oxide is reduced. An excess of carbon monoxide favours a more complete reduction of the ferric oxide. There are several concurrent reactions taking place at the same time. If any water is present in the blast, it will be reduced:



and the nitrogen of the air, brought in with the gas, forms a little cyanogen. The net result is a combustible gas, containing approximately:

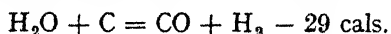
CO	CO <sub>2</sub>	N	H	Hydrocarbons
25.3	10.5	58.1	4.3	1.6 per cent

The combustible gas is utilized for heating the blast; and if there be any surplus, it is used for heating the boilers which run the blowing engine; for calcining the ore, and for general heating purposes. If coal be used in place of coke, tar, etc., separate from the gas at the base of the down-comer and that mixture is treated by the process described under coal gas.

### 3. The Slag

When the charge in the furnace has descended about twenty or thirty feet, and the temperature is about 600°, it has formed a mixture of spongy iron, earthy gangue, coke, and limestone or quicklime. Little further change occurs until the temperature is hot enough to melt the mixture. At this temperature, a fusible slag is formed containing approximately 55 per cent SiO<sub>2</sub>, 30 per cent CaO, and 15 per cent Al<sub>2</sub>O<sub>3</sub>. The fused slag trickles down into the well, and floats on the surface of the molten iron. The slag is either drawn from the furnace at intervals or allowed to run off continuously when it reaches the level of the "slag-hole" and, when cool enough, tipped on the slag heap.

The fact that any water present in the blast is reduced during the operation of the blast furnace has been mentioned. This is a strongly endothermic reaction as shown by the equation:



The heat absorbed in this reaction is taken from that being liberated in the furnace in general and lowers the working temperature, besides using up valuable fuel. Hence, processes for drying the blast are now being tried. One of the most promising methods seems to be the use of silica gel (page 773) which can absorb up to 20 per cent of its weight of moisture, and can be revived simply by heating to a suitable temperature. The gel is made by mixing solutions of sodium hydrogen sulphate and sodium silicate, and is placed on suitable perforated trays in a chamber through which the air for the blast passes. It is interesting to note that if the amount of moisture be reduced below 1.25 grains per cu. ft., the furnace will not operate: a discovery in harmony with the results obtained by Dixon and by Baker on the effects of intensive drying (page 317).

The molten metal which collects on the hearth of the blast furnace is tapped at intervals and run into sand moulds, or into chilled moulds and allowed to solidify. In this form it is known as pig-iron. If it is to be used for steel-making, the charge is sometimes conveyed in the

molten state direct to the converter or furnace in which this is to be done so as to save the cost of fuel required for remelting the solid pig-iron.

Pig-iron is a relatively impure form of iron, containing between 1.5 and 4 per cent of carbon (partly free and partly combined as  $\text{Fe}_3\text{C}$ ) together with phosphorus, sulphur, silicon and traces of other elements. It is a brittle material, and cannot be worked under the hammer, for when heated it passes immediately from the solid brittle condition to the liquid state, when it can be *cast* or poured into moulds; hence after remelting in a vertical furnace, heated by coke and known as a *cupola*, it is known as cast iron. Cast iron is used for the production of a large number of articles of all kinds which do not have to withstand undue strain or shock, among which may be mentioned iron bedsteads, gutter pipes, stoves, railings and similar objects.

#### § 4 Wrought Iron

Wrought iron is practically pure iron and was formerly extensively used on account of its relative freedom from corrosion and excellent welding properties. It has now been very largely superseded by mild steel, although a little is still made for making into welded chains.

Pig-iron is melted on a bed of iron oxide in a reverberatory furnace (Fig. 39.2) and, when molten, the metal is stirred into the bed where the oxide reacts with the impurities. Carbon monoxide is formed which burns on the surface of the molten metal (puddler's candles) and the silicon, manganese and other impurities form a fusible siliceous slag.

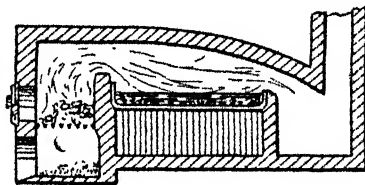


FIG. 39.2.—Reverberatory Furnace (Diagrammatic)

As the metal becomes purer its melting point rises so that it becomes pasty and finally forms "balls" or "blooms" which are spongy in texture and contain considerable amounts of slag. The balls are then removed from the furnace and squeezed as nearly as possible free from slag by working under a steam hammer.

While cast iron melts at about  $1200^{\circ}$ , wrought iron melts at  $1535^{\circ}$ . Wrought iron softens at about  $1000^{\circ}$ , and it can then be forged and welded. Wrought iron is tough and malleable, and fibrous in structure; cast iron is brittle, and it has a crystalline structure. Under the microscope, wrought iron appears to be composed of a bundle of fibres surrounded by some slag of magnetic oxide, etc.; each bundle seems to consist of a series of fibres of metallic iron, interlaced with a little ferrous silicide. These fibres give wrought iron its characteristic structure and enable it to withstand severe longitudinal stresses. Wrought iron was formerly used for shipbuilding, bridge construction and similar purposes, but it has now been largely replaced by mild

steel. A relatively small amount of wrought iron is still made for certain special purposes, such as the making of welded chains, but it represents only a small fraction of the total output of iron.

### § 5 The Manufacture of Steel

By far the largest proportion of the iron produced in modern industry is converted into some form of steel, which is iron containing from 0.1 to 1.5 per cent of carbon, and only the merest traces of sulphur and phosphorus. Other metals (e.g., tungsten, chromium, molybdenum, vanadium, manganese, nickel, cobalt) may be added in considerable quantities for the production of alloy steels for special purposes.

The amount of carbon in steel is thus intermediate between that in cast iron and in wrought iron, so that steel can be made by decarbonizing cast iron or by carbonizing wrought iron. At one time steel was almost entirely made in the latter way; but now only comparatively small quantities are made thus.

The principal methods of making steel are:

- (i) the cementation process;
- (ii) the crucible process;
- (iii) acid and basic Bessemer processes;
- (iv) acid and basic open-hearth (Siemens-Martin) processes;
- (v) electrical processes.

#### The Cementation Process

This process, now virtually obsolete, is the oldest method of steel-making and was the process used in India, Damascus and Toledo. In essence, it is the same as the modern case-hardening process but prolonged to a matter of days in order to introduce larger quantities of carbon into the metal. Bars of specially pure wrought iron—e.g., Swedish iron—are packed with charcoal into sealed firebrick boxes. The boxes are heated in a furnace for eight to eleven days at about 1000°. Carbon monoxide is formed, which diffuses into the hot iron, where it reacts, forming iron carbide ( $\text{Fe}_3\text{C}$ ) which passes into solid solution in the iron. Prolonged heating is necessary owing to the slowness of diffusion in the solid state but eventually the average carbon content is raised to 1 per cent or more. The bars are then removed and subjected to an elaborate forging process in order to distribute the carbon as evenly as possible. It was in this part of the process that the inherited skill of the smiths was shown. Huntsman of Sheffield (1740) conceived the idea of melting the carburized iron in a crucible whereby a uniform distribution of the carbon was achieved more easily.

#### The Crucible Process

Bars of wrought iron are melted with a definite amount of charcoal in fireclay crucibles. The result is a high-grade crucible steel used for

razors, shears and various tools. A less pure product is obtained by heating a mixture of wrought iron with the right amount of cast iron.

This process, also, is now almost obsolete.

### The Bessemer Process

In 1852 Kelly patented a process for purifying pig-iron, based on the fact that if air be forced through a mass of molten pig-iron, in a suitable vessel, the impurities—carbon, silicon, etc.—which prevent the pig-iron being ductile and malleable are oxidized first, and a bath of molten metal, virtually wrought iron, is obtained. In 1856 H. Bessemer patented a converter suitable for the process. Bessemer afterwards bought Kelly's patents. The metal in the converter can be mixed with a known amount of spiegeleisen—i.e., a ferro-manganese containing a known amount of carbon.

The manganese is oxidized by the remaining oxygen of the iron, while the carbon brings the composition of the metal to that of mild steel.

In the Bessemer process about ten tons of molten pig-iron are run into a large egg-shaped vessel, called the *converter* (Fig. 39.3). The converter is made of iron plates lined with siliceous bricks (often *ganister* is used: a silica mineral), and provided with holes at the bottom through which a powerful blast of air can be blown. When the converter has been charged and the blast is turned on, the temperature rises owing to the heat evolved by the oxidation and combustion of the impurities—silicon, manganese and carbon.

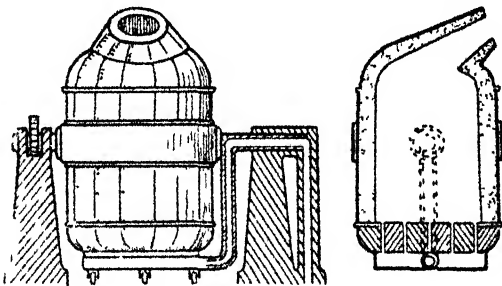


FIG. 39.3.—Bessemer Converter

The carbon forms carbon monoxide, which burns at the mouth of the converter: the other oxides form a slag with the lining. By observing the flame, the right moment to stop the blast can be determined. The right amount of spiegeleisen is then added, the blast is turned on again for a few moments, and the metal is then cast into moulds.

This process revolutionized steel-making when first introduced, and brought down the price of steel from £70 per ton to the neighbourhood of £15, besides making possible the production of very large quantities. Unfortunately, in its original form it can only be employed for pig-iron free from phosphorus, since this, if present, is only oxidized and not removed, and renders the resulting steel brittle and useless.

In 1878, S. G. Thomas and P. C. Gilchrist showed that, if the converter be lined with, say, dolomite (basic lining) and some lime be

added to the charge of pig-iron, and the blast continued a little longer, the oxides of phosphorus, sulphur and silicon formed combine with the lime. The operation is otherwise conducted as before. The process gives rise to *basic slag*, which is used as a fertilizer on account of the phosphorus it contains. If the lining is siliceous, the operation is called the *acid Bessemer process*; and if dolomite, the *basic Bessemer process*.

### The Siemens-Martin Open-hearth Process

This is now the method in widest use for the manufacture of steel.

In this process, the furnace is charged with a mixture of pig-iron, scrap iron and good haematite ore free from carbon. The mixture is melted in a shallow rectangular trough or hearth. The furnace is heated by producer gas. Both the gas and the secondary air for the combustion of the gas are pre-heated so that a very high temperature can be obtained. A general idea of the process can be gathered from Fig. 39.4,

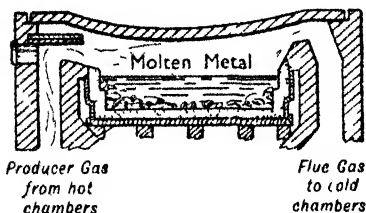


FIG 39.4 --Hearth of Siemens-Martin Process (Diagrammatic)

which shows a section through the hearth. The air port is not shown in the diagram. The gas and air burn on the left, the flue gases travel down the flue on the right, and in doing so heat up two chambers packed with checker brickwork. The direction of the burning gas is then reversed. Gas and air pass separately through the heated chambers, and the flue gases heat up another pair of similar chambers below the hearth. The direction travelled by the burning gas is reversed about every half-hour, and the heat of the flue gases is utilized in warming up chambers through which the unburnt gas and air will pass later on. The furnace is called *Siemens' regenerative furnace*. When a test shows that the metal contains the right amount of carbon, ferro-manganese is added as in the case of Bessemer's steel. If the bed of the furnace is made of siliceous materials—*acid process*—the proportions of carbon, silicon, and manganese are reduced during the treatment, but the amounts of sulphur and phosphorus remain fairly constant. In the *basic process*, the furnace is bedded with, say, dolomite, and there is a steady fall in the amount of phosphorus and sulphur during the treatment, just as was the case with the basic Bessemer process.

The open-hearth process owes its commanding position in the steel industry to the readiness with which the composition of the steel can be controlled, the uniformity of the product, the ability to use up steel scrap, the relatively smaller loss of iron in the process (4 per cent as against 15 per cent in Bessemer), and the large quantities which can be dealt with at one operation. Its principal disadvantage, in comparison

with the Bessemer process, is the necessity for heating the furnace externally, and the length of time required to complete a charge: 10 hours or so (as compared with 20 minutes).

### Electrical Processes

Electric furnaces, often of the arc-type, are used in the production of special high-quality steels. The absence of contact with furnace-gases reduces the chance of contamination by impurities and lessens the risk of the finished product containing "blow-holes." The purity of the product renders these methods important, especially where electric power is cheap as in Sweden, for the manufacture of high-grade products and special alloy steels.

For making high-class steels the high-frequency induction furnace is coming into increasing use. The heat is generated within the metal itself by induced eddy currents and very high temperatures can be attained. Another advantage of the high-frequency furnace is the automatic stirring which is brought about by the movement of the metal under the influence of the induced currents.

## § 6 The Constitution and Properties of Iron and Steel

Pure iron is a laboratory curiosity; all commercial forms of iron contain impurities, notably carbon; and their properties depend upon the nature and amount of these impurities.

Iron appears to exist in several allotropic modifications and it is unique among the metals in that almost the whole of its industrial importance depends upon allotropic changes. Other metals are known to exist in more than one allotropic form but, with the exception of tin, the changes are small and the physical and chemical properties of the allotropes are so nearly identical that their allotropy is of scientific, and not technical, importance. In the case of iron, however, the properties of the allotropes are widely different in several important respects, notably in their capacity for dissolving carbon, and as all industry is at present based on steel a knowledge of the allotropy of iron is evidently of first importance.

Pure iron freezes at  $1535^{\circ}$ , and the crystals formed at this temperature have a body-centred cubic lattice. At  $1403^{\circ}$  this lattice changes to the face-centred form which, at  $906^{\circ}$ , changes back again to the body-centred one. Iron in these three thermal regions is known as  $\delta$ -,  $\gamma$ - and  $\alpha$ -iron respectively and the change points as the  $A_4$  and  $A_3$  points. ("A" is from the French *arrêt*, a rest or halt, because of the halts on the time-temperature, or cooling, curve at these points.) These changes are reversible but the achievement of equilibrium is so slow that even with extremely gradual heating or cooling there is always a time lag. This "thermal hysteresis" may amount to as much as  $50^{\circ}$  to  $100^{\circ}$  and when it is necessary to distinguish between the two cases the suffix letters "c" and "r" are used (derived from the

French *chauffage, refroidissement*). Thus  $Ac_3$  means the change point  $\alpha \rightarrow \gamma$  when heating and  $Ar_3$  means the  $\gamma \rightarrow \alpha$  change on cooling.

There is another type of change which takes place at  $768^\circ$  and which is also reversible, for at this temperature the iron atom changes to the paramagnetic state. A small alteration in specific heat also occurs at this point so that there is another halt on the cooling curve. This used to be known as the  $A_2$  point and iron between  $768^\circ$  and  $906^\circ$  was called  $\beta$ -iron, but as it is now known that there is no phase change  $\beta$ -iron is no longer believed to be a separate allotrope. The thermal change which accompanies the magnetic transformation is the cause of *recalcescence*, i.e., the sudden brighter glow of the slowly cooling metal (Barrett, 1874).

It is now believed that  $\delta$ -iron is a reappearance of  $\alpha$ -iron and not a separate phase. This view is supported by the fact that if the specific volume-temperature curve for  $\alpha$ -iron is extrapolated beyond  $906^\circ$  it is found to coincide with the corresponding curve for  $\delta$ -iron, and also by the observation that the addition of certain alloying elements to iron, e.g., silicon, chromium or phosphorus, causes the contraction of the  $\gamma$ -region and the enlargement of the  $\delta$ -region until they are no longer separated by a phase boundary.

The discussion, so far, applies to the pure element only and is of great theoretical interest but the modifications produced by the addition of carbon are of much greater practical importance while the theoretical interest remains. Liquid iron will dissolve up to about 5 per cent of carbon but in the solid state the solubility is very much smaller. When the metal freezes some of the carbon is, therefore, rejected from solution either as **cementite**, which is iron carbide,  $Fe_3C$ , or, if it exceeds about 1.7 per cent, as graphite, which may be formed directly by crystallization from the solution or indirectly by decomposition of cementite. The iron end of the iron-carbon phase rule diagram is given in Fig. 39.5.

If Fig. 39.5 be compared with Fig. 13.4 (page 184) it can be seen that there are three separate sets of equilibria, viz., (i) the system ACD, ECF which relates to the freezing of molten alloys of carbon and iron; (ii) the system GSE, PSK which relates to a series of changes occurring in the solid alloys; and (iii) the system ABN, known as the  $\delta$ -tip.

Neglecting for the moment the  $\delta$ -tip, the diagram is interpreted as follows. A(B)C represents the temperatures at which crystals of  $\gamma$ -iron containing carbon in solid solution and known as **austenite** (after Sir W. Roberts-Austen) begin to separate; the curve A(J)EC represents temperatures at which this freezing process is complete and these two curves are known as the *liquidus* and *solidus* respectively. Similarly, CD (*liquidus*) and CF (*solidus*) represent the beginning and completion of the freezing of the carbide (**cementite**). It will be seen that austenite and cementite form a eutectic, when the percentage of carbon is 4.3, which freezes at  $1130^\circ$ .



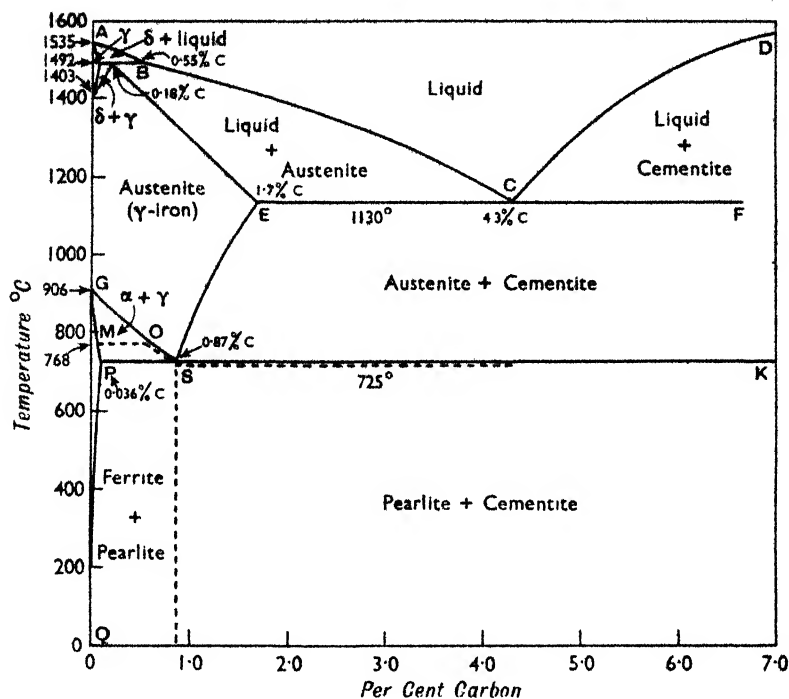


FIG. 39.5 -- The Iron-Carbon System

In the second (solid solution) system GS represents the commencement of the  $\gamma \rightarrow \alpha$  allotropic change while GPS represents its completion. (Cf. AC and AEC.) ES represents the commencement of the separation of cementite from the solid solution (austenite) and SK represents its completion. (Cf. CD and CF.) Just as the freezing point is lowered, as shown by BC, when the percentage of carbon is increased (cf. AO in Fig. 13.4) so the temperature at which the allotropic change occurs is also lowered as the amount of carbon in solid solution increases. Furthermore, PSK is a eutectoid line and S a eutectoid point. At S  $\alpha$ -iron (known as **ferrite**) and the carbide,  $\text{Fe}_3\text{C}$  (cementite), are produced simultaneously from the solid solution (austenite) yielding a eutectoid, consisting of minute parallel plates of the two phases, known as **pearlite**. This was originally called *pearlyite* by its discoverer, Dr. H. C. Sorby of Sheffield, on account of its "mother-of-pearl" iridescence when viewed under the microscope by oblique illumination. The composition of this eutectoid corresponds to 0.87 per cent of carbon and at this point, and on the broken vertical line below it, the steel consists entirely of pearlite. To the left of this line the structure is

pearlite plus ferrite (hypo-eutectoid) and to the right it is pearlite plus cementite (hyper-eutectoid).

The  $\delta$ -tip may be interpreted thus.  $\delta$ -iron freezes out at  $1535^\circ$  and, on cooling to  $1492^\circ$ , a peritectic reaction takes place, the  $\delta$ -iron plus liquid becoming  $\delta + \gamma$  (all solid). Between  $1492^\circ$  and  $1403^\circ$   $\delta$ -iron is progressively converted into  $\gamma$ -iron and ultimately disappears (line JN); the point J corresponding to the presence of 0.18 per cent of carbon.

The area GPQ, which does not correspond to anything in Fig. 13.4, represents the (very small) solubility of carbon in  $\alpha$ -iron (ferrite) amounting to a maximum of 0.35 per cent at the eutectoid temperature, falling to 0.003 per cent at ordinary temperature. The dotted line MOSK represents the magnetic change (Curie points).

In all the preceding discussion it has been assumed that the rate of cooling is sufficiently slow to allow of equilibrium being established at each stage, a condition which is of particular importance in the region between GSE and PSK, which is known as the **critical range**. As an example the effect of heating, in this way, a steel containing 0.4 per cent of carbon may be considered. This, in equilibrium, consists of approximately equal amounts of ferrite ( $\alpha$ -iron) and pearlite. When this is slowly heated to  $725^\circ$ , the  $A_1$  point ( $A_{c1}$  point), the face-centred lattice of  $\alpha$ -iron begins to change to the body-centred one of  $\gamma$ -iron and this involves also a change in the volume of the unit crystal. At the same time the carbon, which has been practically exclusively confined to the cementite constituent of the pearlite, begins to diffuse into the almost carbonless (now  $\gamma$ -) iron which surrounds it. This process is analogous to the diffusion of any solute from a region of high to a region of low concentration except that it is very much slower when it takes place as here in the solid state. The cementite, therefore, disappears and the final state at any temperature within the area GSEA is a uniform solid solution of 0.4 per cent of carbon in  $\gamma$ -iron (i.e., austenite). With slow cooling the reverse process takes place. When the temperature falls to a point on the line GS the  $\gamma$ -iron begins to change into  $\alpha$ -iron and the carbon is rejected from the solid solution in the form of cementite ( $\text{Fe}_3\text{C}$ ). This process continues until the concentration of carbon in the remaining solid solution reaches 0.87 per cent when ferrite and cementite are formed simultaneously at constant temperature as the eutectoid pearlite.

If instead of very slow cooling the cooling process is accelerated so that equilibrium cannot be established the  $\alpha$ -iron has no time to separate, the carbon is unable to diffuse quickly enough and the phase boundary is reached too soon. The resulting structure then shows abnormally large areas of pearlite and correspondingly small areas of  $\alpha$ -iron and, with more rapid cooling, a steel containing more than about 0.4 per cent of carbon may appear to be entirely pearlitic.

A rate of cooling of about  $35^\circ$  per second suppresses the pearlite change altogether and the resulting structure shows varying small amounts of austenite and a new constituent known as **martensite** (after

A. Martens). The relative amounts of these two phases depend on the rate of cooling and on the quantity of carbon present; faster cooling and high carbon content tend to cause the retention of more austenite and concomitant formation of less martensite but even with a rate of cooling as high as  $3000^{\circ}$  per second it is impossible to retain more than 50 to 60 per cent of austenite. But an ordinary industrial "quench" in water (about  $100^{\circ}$  per second) is sufficient to suppress the formation of pearlite and give a purely martensitic structure.

The exact nature of martensite has been much disputed. High carbon martensite, as quenched, is intensely hard and extremely brittle; it is, moreover, magnetic, so that it cannot be a form of austenite which, with the same carbon content, is relatively soft and ductile and non-magnetic. The present view is that it is a "forced" solution of carbon in  $\alpha$ -iron and that its intense hardness is caused partly by suppressed volume changes and partly by the precipitation of cementite, possibly in a state of almost molecular dispersion upon the principal crystallographic planes of the lattice.

Metals deform by the lateral movement of lattice-layers along certain preferred crystal planes. Such movement usually occurs quite easily in the pure metal but it is impeded if, for any reason, the lattice is not quite uniform, as, for example, if alien atoms of the "wrong" size are present. This occurs when small quantities of a second metal are present in solid solution; the rows of atoms in the lattice become bent and its planes buckled and distorted so that easy slipping is prevented and we say that the metal has been hardened and strengthened by alloying.

Very much the same thing would occur if small, hard particles were deposited on these planes (compare the effect of sand on a slide or of grit in a bearing), and it is believed that this is the case with martensite. Martensite must be, essentially, a form of  $\alpha$ -iron because it is magnetic and its space lattice as revealed by X-rays is a very slightly distorted form of that of  $\alpha$ -iron. But carbon is almost completely insoluble in  $\alpha$ -iron whereas martensite may contain up to 1.7 per cent of carbon, and yet as this does not appear as a separate phase either under the microscope or in X-ray examination it must be in some sort of solution. This difficulty has proved a great obstacle to the understanding of the nature of martensite and it was only when the close analogy between the phenomena under discussion and those associated with colloidal solutions was properly realized that the difficulty was cleared up. The carbon in austenite is in true solution while that in martensite is in colloidal solution.

Although austenite and martensite are both metastable below  $A_{r1}$ , the metal is so rigid that no perceptible change takes place at ordinary temperatures even in the course of centuries. On heating, this rigidity is relaxed so that breakdown into stable forms takes place. This is what happens in the process of **tempering**. When martensite is tempered at temperatures below the critical range no changes are visible under the microscope but the original intense hardness and brittleness are

slightly reduced. Raising the temperature and keeping it up for a longer time continues this process, releasing the internal stresses and coagulating the precipitating cementite from its original high degree of dispersion until the point is reached at which pearlite makes its appearance. Formed in this way, however, it is so unlike ordinary pearlite that it has always been known as **troostite** (after L. Troost) and it is only latterly that it has been shown to be an extremely finely divided "emulsion" of ferrite and cementite.

Continuing the tempering process causes the precipitate to become coarser and to coagulate still further, through a stage once known as sorbite (after H. C. Sorby) but now as *granular* or *emulsified* pearlite, until it emerges finally as the ordinary laminated constituent characteristic of fully tempered (or annealed) steels.

Troostite, sorbite and pearlite are all essentially the same, viz., separate particles or layers of ferrite and cementite, the differences being of degree and not of kind. The series martensite, troostite, sorbite and pearlite is analogous to a colloidal solution of sulphur in water which is at first clear and water-white and then, as the disperse phase coagulates, passes through the stages of interference effects, or opalescence to the final one of visible precipitation.

Retained austenite behaves similarly. The final result of its tempering is to produce troostite but at the same time, above about  $400^{\circ}$ , martensite is formed. The final result is, therefore, identical, although the mechanism is not the same.

The principles underlying the commercial heat-treatment of steel can now be understood. Heating up through the critical range produces greater uniformity and refinement of the metal structure on account of the recrystallization involved in the  $\alpha \rightarrow \gamma$  phase change and the subsequent solution of the carbon. Subsequent cooling, at rates not too far removed from the equilibrium rate, fixes the refined structure and produces marked improvement in the physical properties of large forgings and castings. This process, viz., heating up to just above  $A_{c3}$ , holding there until the carbides have had time to pass into uniform solid solution and then cooling in air, is known as **normalizing**. Cooling the steel from above  $A_3$  at speeds in excess of the critical rate, e.g., by quenching in water, oil, or an air blast, produces martensite, and when this is suitably tempered below  $A_3$  in order to remove quenching stresses and to restore some measure of ductility the metal is suitable for use in cutting tools or springs. Prolonged tempering at, or near,  $A_{c1}$ , followed by very slow cooling, is called **annealing**. Annealed steel is relatively soft, weak and ductile and the metal is used in this condition when it is required to undergo cold deformation in the course of a fabrication process. Forging is the process of fabrication by hot deformation under the hammer or in a press. The steel is heated well above  $A_c$  when it becomes plastic; it is then worked under the hammer until its temperature falls below red heat ( $A_r$ , approx.); the deformation serves to prevent the injurious grain growth which would otherwise occur.

### Alloys of Iron

Iron forms many valuable alloys with other elements, particularly in the form of special steels. Among the alloying elements may be mentioned vanadium, titanium, chromium, molybdenum, tungsten, manganese, nickel and cobalt. These, and their properties, are referred to briefly under the heading of the element concerned. In addition, the presence of more than the normal proportion of silicon produces a material of remarkable resistance to acids and other reagents, but it is very brittle and is not to be regarded as a steel. In certain circumstances silicon-steels can be made (see page 768).

In addition to the processes of hardening, annealing and tempering, which affect the whole body of the metal, the methods of **case-hardening**, **nitriding** and the **Barff process** are applied to the surface of finished articles.

**Case-hardening** of wrought iron or mild steel is effected by heating the metal in contact with carbon or potassium ferrocyanide thereby producing a hard steel surface. **Nitriding** is carried out by passing dry ammonia gas over the metal parts heated to  $500^{\circ}$  in sealed boxes for 90 hours. An intensely hard surface skin is produced with practically no change in volume. The degree of hardness is much greater than that produced by case-hardening and the method has the additional advantage that the temperature required is below the critical range of steel. In the **Barff process** the metal is heated to redness and steam is passed over it, so that an adherent surface layer of ferrous oxide is produced. This process has been suggested, *inter alia*, for treating cans for food preservation as an alternative to tinning.

### Properties of Pure Iron

Pure iron is a grey, lustrous metal which crystallizes in the cubic system. It melts at  $1537^{\circ}$ , and boils at  $2800^{\circ}$ ; its density is 7.87 and its specific heat 0.11. One of the most noteworthy of the physical properties of iron is its magnetism. All elements exhibit some slight magnetic phenomena; but the diamagnetism of iron is remarkable and almost unique, being more than a million times greater than that of any other element except nickel and cobalt. Diamagnetism is possessed only by  $\alpha$ -ferrite;  $\gamma$ -ferrite is feebly paramagnetic.

Iron is readily oxidized; it burns brilliantly in oxygen, and, when finely divided, will also burn in air, the magnetic oxide ( $\text{Fe}_3\text{O}_4$ ) being formed. Iron also burns in chlorine and in sulphur vapour; ferric chloride and ferrous sulphide being the respective products. When heated to redness, iron also reacts readily with steam, hydrogen and the magnetic oxide resulting.

Iron dissolves in dilute acids; sulphuric acid furnishes ferrous sulphate and hydrogen; and hydrochloric acid furnishes ferrous chloride and hydrogen. With cold dilute nitric acid (specific gravity below 1.034) hydrogen is not evolved, but the acid is reduced to

ammonia, and this reacts with the excess of nitric acid to form ammonium nitrate; with an acid of specific gravity 1.034 to 1.115, *ferrous nitrate* is the main product; and with an acid of greater specific gravity than 1.115, say 1.3, *ferric nitrate* is the main product. With concentrated nitric acid (specific gravity 1.45), the iron does not appear to react. The iron in contact with the concentrated acid appears to have changed, for it behaves differently from a piece of the same sample of iron which has not been in contact with concentrated nitric acid. The sample which has not been in contact with the strong acid will precipitate copper from copper sulphate solutions, lead from lead nitrate, and silver from silver nitrate; the other sample will not. The inert iron is said to be in the passive condition. **Passive iron** does not react when dipped in dilute nitric acid. Other oxidizing agents, chromic acid, hydrogen peroxide, will make iron passive. The cause of passivity is that a thin film of oxide is formed on the metal by contact with the oxidizing agent. This has been proved by electron diffraction experiments and by the isolation of the film of  $\text{Fe}_2\text{O}_3$ . (Evans.) The passivity can be removed by scratching the surface of the iron, by heating it in a reducing gas, by strongly rubbing the surface, and by bringing the passive iron in contact with zinc while immersed in the dilute nitric acid. Other metals also exhibit passivity, e.g., cobalt, nickel, chromium, and bismuth.

Iron is not appreciably attacked by alkalis, except at high temperatures.

### The Rusting of Iron

It has been estimated that the world's annual loss by corrosion of iron, steel and the ferrous metals generally, is in the neighbourhood of 700 million sterling (Hadfield). It is, therefore, evident that the problem of the protection of iron and steel articles, so as to render them resistant to corrosion, is of paramount importance.

When commercial iron is exposed to a humid atmosphere for a short time, it soon becomes covered with a reddish-brown film which is called *rust*. Iron rust seems to be an indefinite mixture which on analysis furnishes numbers which vary according to the age of the rust, etc. Rust usually contains ferrous oxide, ferric oxide, carbon dioxide, and water. Analyses show that rust is probably a mixture of ferric oxide, hydrated ferrous and ferric oxides, and basic ferrous and ferric carbonates. If the rust has been long exposed to the air, the amount of ferric oxide is relatively large, and the amounts of ferrous oxide and carbon dioxide small. Rusting is a complex process, and workers are by no means agreed on the simple facts. Dry iron in dry air does not rust, moisture must be present before rusting can occur.

It also appears to be true that water alone (in the absence of air) will not cause rusting to take place. There is still some dispute as to whether pure iron will rust in the presence of pure water and pure oxygen only, and although it is quite possible that rusting does not

occur under these conditions, nevertheless, this particular question is of academic interest only.

Some deny, others affirm, that the presence of an acid and water are necessary. It is exceedingly difficult to free water and the surface of glass from carbon dioxide; and silicic acid can be dissolved from the glass vessels used and from particles of slag in the iron. However, where careful attention has been taken to eliminate the disturbing factors, the evidence seems in favour of the conclusion that the presence of an acid is necessary for rusting; that an acid is always present when the iron dissolves; and it is highly probable that pure iron does not undergo appreciable oxidation when exposed to pure water and to pure oxygen. Films of moisture frequently condense on the surface of iron exposed to the air, and the moisture holds carbon dioxide and oxygen in solution. The mechanism of the "atmospheric rusting" of iron may then proceed according to the following scheme: An acid ferrous carbonate,  $\text{Fe}(\text{HCO}_3)_2$ ; or a basic carbonate,  $\text{Fe}(\text{OH})(\text{HCO}_3)$ , is first formed. The ferrous carbonate in contact with oxygen is oxidized to basic ferric carbonate,  $\text{Fe}(\text{OH})_2(\text{HCO}_3)$ ; or to  $\text{Fe}(\text{OH})(\text{HCO}_3)_2$ ; or both. The basic ferric carbonate is then hydrolysed by the water, forming ferric hydroxide,  $\text{Fe}(\text{OH})_3$ ; and the ferric hydroxide is subsequently more or less dehydrated, forming ferric oxide. Ferric oxide is more or less hygroscopic, so that once rusting has started, at any point, subsequent corrosion is quicker because the ferric oxide helps to keep the surface of the iron adjacent to the rust spot moist. Several other hypotheses have been suggested, and the subject is still *sub judice*.

It has been shown by U. R. Evans that an important cause of the rusting of iron is differential aeration, and in so doing he has provided an explanation of the peculiar phenomenon of pitting. It is fairly clear that the corrosion of iron is an electro-chemical phenomenon connected with the different electrical condition of different portions of the metal; for, if one piece of a metal becomes electropositive to another, that piece will dissolve more rapidly in contact with an electrolyte, just as pure zinc dissolves more readily in acids when in contact with copper. If a cell be made in which the electrodes are two portions of iron, one of which is immersed in air-free water, and the other in water through which air is bubbled, a current is found to flow and the iron which is screened from air dissolves. Thus corrosion occurs at a point which is most screened from the air and so rusting, having once started, will tend to be worst at the deepest point in a rust patch, thus producing pits.

### Atomic Weight

The values found for the vapour densities of volatile compounds of iron, such as iron carbonyls and ferric chloride, and the specific heat (0.116), indicate a value in the neighbourhood of 56 for the atomic weight of iron.

Accurate values have been determined by conversion of pure ferrous

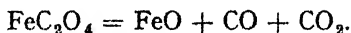
chloride and bromide into silver chloride and bromide, and by reduction of pure ferric oxide in a stream of hydrogen. By the bromide method Hönigschmid obtained values between 55.847 and 55.854. The mean of eighteen experiments is 55.85, and this is the value recommended by the International Committee at the present time (1957).

### § 7 Oxides and Hydroxides of Iron

Iron forms three oxides, viz.:

Ferrous oxide,  $\text{FeO}$ ;  
 Ferrosic oxide (magnetic oxide),  $\text{Fe}_3\text{O}_4$ ;  
 Ferric oxide,  $\text{Fe}_2\text{O}_3$ .

**Ferrous oxide**,  $\text{FeO}$ , is formed when ferric oxide is heated in hydrogen at  $300^\circ$  or in a mixture of equal volumes of carbon monoxide and dioxide at  $800^\circ$ . It is also formed when ferrous oxalate is heated out of contact with the air:



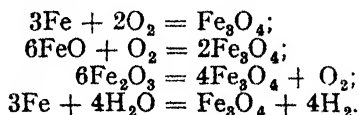
When exposed to the air, it oxidizes readily, sometimes burning spontaneously, to ferric oxide. It is a basic oxide, and dissolves readily in acids forming ferrous salts.

**Ferrous hydroxide**,  $\text{Fe}(\text{OH})_2$ , is obtained as a white precipitate when solutions of alkali hydroxides or ammonia are added to a solution of ferrous salt, with complete exclusion of air. If the solutions contain dissolved air, the precipitate has a greenish colour. It rapidly absorbs oxygen and passes into brown ferric hydroxide. It reacts readily with acids, forming solutions of ferrous salts.

#### **Ferrosic Oxide, Magnetic Oxide of Iron, $\text{Fe}_3\text{O}_4$**

This compound occurs in nature as the mineral *magnetite* in black, octahedral crystals which are magnetic.

It is the most stable oxide, and is formed when iron or iron oxides are heated in air or oxygen, or when steam is passed over red-hot iron.



According to Moissan, there are two modifications of ferrosic oxide: the one is formed by heating ferric oxide from  $350^\circ$  to  $400^\circ$  in a current of hydrogen or carbon monoxide; and the other by reactions at a high temperature, e.g., the combustion of iron in oxygen. The former is attacked by nitric acid, and has a specific gravity of 4.86; the latter is not attacked by the same acid, and has a specific gravity 5.0 to 5.1. The phenomenon is thus analogous with the general effect of high temperatures on oxides like alumina, chromic oxide, ferric oxide, etc.



Ferrosic oxide is not a basic oxide since it forms a mixture of ferric and ferrous salts when treated with acids. It is probably a "compound" oxide, analogous to manganosic oxide,  $\text{Mn}_3\text{O}_4$ , and red lead,  $\text{Pb}_3\text{O}_4$ .

On this assumption, ferrosic oxide is a *ferrous ferrite*,  $\text{Fe}(\text{FeO}_2)_2$ . Several other ferrites are known (see below).

**Ferric oxide**,  $\text{Fe}_2\text{O}_3$ , occurs naturally in large quantities as *haematite* and *specular iron ore*—a crystalline form. It is obtained as one of the products of the roasting of iron pyrites for the manufacture of sulphuric acid (page 465). It is formed as a reddish-brown powder when ferrous sulphate, or carbonate, or hydroxide, or many organic salts of iron are calcined in air. It is stable at a red heat, but at temperatures above about  $1300^\circ$  it decomposes into  $\text{Fe}_3\text{O}_4$ . It is reduced to iron by hydrogen at  $1000^\circ$ .

The finely divided oxide obtained by calcining ferrous sulphate is known as *jeweller's rouge* and is used as a pigment. *Red ochre* and *venetian red* are also forms of ferric oxide. The particular tint of the pigment depends upon the temperature of calcination, which appears to determine the size of the particles.

When prepared at a low temperature, ferric oxide dissolves fairly easily in acids, forming ferric salts; but if it be heated to a temperature above  $600^\circ$ , acids only attack it with difficulty.

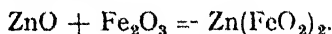
### Ferric Hydroxides

A voluminous red-brown precipitate is formed when ammonium hydroxide is added to a solution of a ferric salt, and this appears to be the fully hydrated oxide,  $\text{Fe}(\text{OH})_3$ . On drying and heating, this passes into ferric oxide. It readily reacts with acids, forming solutions of ferric salts, although it is a very weak base and its salts are largely hydrolysed in solution.

Ferric hydroxide can readily be obtained in the form of a colloidal solution as described on page 278.

A hydrate of the composition  $\text{FeO}(\text{OH})$  or  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$  occurs naturally as the mineral gothite, and is also obtained by the action of water on sodium ferrite. It may be **ferrous acid**,  $\text{HFeO}_2$ .

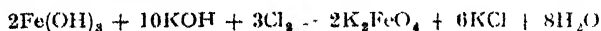
On heating an intimate mixture of ferric oxide with sodium carbonate, **sodium ferrite**,  $\text{NaFeO}_2$ , is formed. Similarly, other ferrites result when ferric oxide is heated with basic oxides, e.g.:



In these reactions ferric oxide exhibits an acidic character: it is thus an amphoteric oxide like aluminium oxide and chromic oxide.

### Ferrates

When chlorine is passed through a concentrated solution of potassium hydroxide in which ferric hydroxide is suspended, the solution assumes a purple colour, and a black powder of **potassium ferrate**,  $\text{K}_2\text{FeO}_4$ , separates. The reaction is usually represented:



The black powder appears to be analogous to potassium manganate,  $K_2MnO_4$ , with potassium chromate,  $K_2CrO_4$ , and with potassium sulphate,  $K_2SO_4$ . The salt dissolves in water, forming a rose-red solution which, on crystallization, furnishes dark-red crystals isomorphous with potassium sulphate and chromate. Potassium ferrate is unstable and its solution readily decomposes:



The barium salt,  $BaFeO_4$ , is a dark carmine-red and fairly stable. By analogy with the chromates and sulphates, it is inferred that the ferrates are derived from an unknown ferric acid,  $H_2FeO_4$ ; which in turn is derived from an unknown ferric anhydride,  $FeO_3$ , analogous with sulphur and chromic trioxides.

## § 8 Salts of Iron. Ferrous Salts

Iron forms two series of salts derived respectively from ferrous oxide and ferric oxide.

### Ferrous Salts

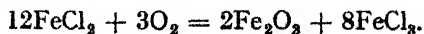
The ferrous salts are usually colourless when anhydrous, and form green crystalline hydrates and faintly green solutions. They are readily oxidized in acid solution by most oxidizing agents and, hence, are useful reducing agents. They are stable in air in presence of acid, but otherwise are readily oxidized in contact with the atmosphere. This probably occurs through the formation of the hydroxide which is precipitated in alkaline solutions, and is present in neutral solutions on account of hydrolysis.

Ferrous salts are distinguished from ferric salts in that they give a green precipitate with ammonia or alkali solutions, and a blue precipitate of Turnbull's blue with potassium ferricyanide solution (see page 928).

**Ferrous carbonate**,  $FeCO_3$ , occurs naturally as *spathic iron ore*, and can be obtained as a white precipitate by mixing air-free solutions of sodium carbonate and ferrous sulphate. It rapidly oxidizes in contact with the air, becoming green, and finally red, through formation of ferric hydroxide.

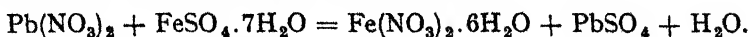
**Ferrous chloride**,  $FeCl_2$ , is obtained in solution by dissolving pure iron wire in dilute hydrochloric acid. On concentration, the solution deposits bluish-green crystals having the composition  $FeCl_2 \cdot 4H_2O$ . On heating, it decomposes so that the anhydrous salt cannot be obtained in this way. This is made by passing dry hydrogen chloride over heated iron, using the apparatus indicated in Fig. 39.6, when white feathery crystals are produced.

Ferrous chloride is very soluble in water (100 grams of water dissolve 67 grams of anhydrous salt at  $15^\circ C.$ ), and the solution has an acid reaction, probably on account of hydrolysis. Like the sulphate, the solution absorbs nitric oxide forming a black or very dark brown solution. On heating in air, ferrous chloride decomposes into ferric oxide and chloride:



With ammonia gas, at room temperatures, ferrous chloride forms  $\text{FeCl}_2 \cdot 6\text{NH}_3$ , which passes into  $\text{FeCl}_2 \cdot 2\text{NH}_3$  at about  $300^\circ$ . It readily forms double salts, of which  $\text{FeCl}_2 \cdot 2\text{NH}_4\text{Cl}$ —or  $(\text{NH}_4)_2\text{FeCl}_4$ —ferrous ammonium chloride is the most important.

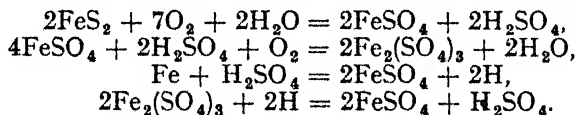
**Ferrous nitrate**,  $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , forms unstable green crystals. It is obtained by grinding together equivalent quantities of ferrous sulphate and lead nitrate with a little alcohol:



**Ferrous sulphide**,  $\text{FeS}$ , is made by heating iron filings and sulphur, considerable heat being evolved in the process; or by dipping iron rods into molten sulphur. It is precipitated when hydrogen sulphide is passed into alkaline solutions of ferrous salts and when colourless ammonium sulphide solution is added to a solution of a ferrous salt. It is a black, insoluble substance with a metallic lustre in mass. It readily reacts with dilute acids, yielding hydrogen sulphide, and is used for the preparation of this gas (page 482).

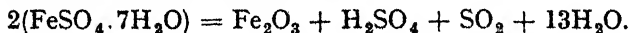
### Ferrous Sulphate, Green Vitriol, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

Ferrous sulphate occurs native as *copperas* or *melanterite*. It was known to the Ancient World and used for making ink, and in medicine. It is still used for the former purpose; also for the preparation of blue pigments, and as a mordant. It is made commercially from iron pyrites. This is stacked in heaps exposed to air and moisture. Oxidation occurs, and the liquid which drains away contains ferrous and ferric sulphates and sulphuric acid; the "drainage solution" is converted into ferrous sulphate by scrap iron; on crystallization, the solution furnishes pale green, rhombic prisms of the composition  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ .



Pure ferrous sulphate is made in the laboratory by dissolving pure iron in dilute sulphuric acid, precautions being taken to exclude air.

Ferrous sulphate, prepared as above, is a green crystalline solid, soluble in water (100 grams of water dissolve 43.5 grams of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  at  $15^\circ$ ). On heating, it decomposes, losing water and forming sulphur dioxide and sulphuric acid (page 496):



This reaction was at one period used for making sulphuric acid. On exposure to the air, the crystals turn brown, presumably owing to the formation of a basic ferric sulphate. Solutions of ferrous sulphate absorb nitric oxide, forming a black or dark-brown solution, a property made use of in the brown-ring test for nitrates (page 453), and in the preparation of nitric oxide (page 460).

Ferrous sulphate crystals are isomorphous with the corresponding salts of beryllium, magnesium, zinc, cadmium, manganese, chromium, cobalt and nickel, all of which crystallize with seven molecules of water. These are known as vitriols, e.g., green vitriol is ferrous sulphate; white vitriol, zinc sulphate. It is interesting to note that copper sulphate normally crystallizes with  $5\text{H}_2\text{O}$ , but a salt isomorphous with the above series and of the composition  $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ , is formed when copper sulphate in admixture with the sulphate of iron, zinc or magnesium, is allowed to crystallize.

**Ferrous ammonium sulphate, Mohr's salt,**  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , is made by dissolving equi-molecular quantities of ammonium sulphate and of ferrous sulphate in the least possible quantities of hot water (at  $60\text{--}70^\circ$ ), mixing the hot solutions and adding a trace of dilute sulphuric acid. Pale green crystals of the double salt separate on cooling. It is soluble in water (100 grams of water dissolve 20 grams of the salt at  $15^\circ$ ), and both the solid and solution are less readily oxidized by contact with the atmosphere than ferrous sulphate, particularly when precipitated by adding alcohol to the concentrated aqueous solution and washing with alcohol. It is used in volumetric analysis.

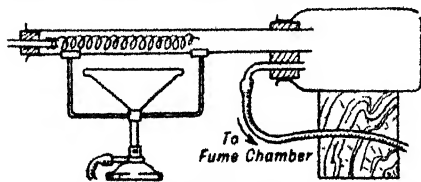
**Ferrous chloride,**  $\text{Fe}_2\text{Cl}_6 \cdot 10\text{H}_2\text{O}$ , is analogous in composition to the magnetic oxide. It is made by dissolving that oxide in concentrated hydrochloric acid and evaporating the solution in a desiccator containing concentrated sulphuric acid. It forms yellow deliquescent crystals.

### § 9 Ferric Salts

The ferric salts are usually yellow, although in solution they often appear darker on account of the formation of ferric hydroxide by hydrolysis. They are found to be more easily hydrolysed than the ferrous salts, i.e., ferric hydroxide is a weaker base than ferrous hydroxide.

Ferric salts are readily reduced to the corresponding ferrous salts by many reducing agents, e.g., nascent hydrogen, sulphur dioxide, etc. They are thus weak oxidizing agents. Some ferric salts (e.g., the oxalate) are reduced by the action of light; a fact which is made use of in the blue-print process for reproducing diagrams, etc.

#### Ferric Chloride, $\text{FeCl}_3$ or $\text{Fe}_2\text{Cl}_6$



Anhydrous ferric chloride is made by passing dry chlorine over iron heated in a combustion tube. The ferric chloride formed is volatile and can be condensed in a bottle attached to the outlet of the tube. (See Fig. 39.6.) It forms glistening

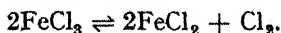
FIG. 39.6—Preparation of Ferric Chloride.

scales which appear greenish by reflected light, and dark red by transmitted light.

Ferric chloride is ordinarily met with in the hydrated form, which is prepared by the action of iron, ferrous carbonate or ferric oxide on hydrochloric acid, to which a little nitric acid has been added. Several hydrates are known; the one formed by allowing the solution made as above to crystallize has the composition  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .

Ferric chloride is very soluble in water (100 grams of water dissolve 92 grams of the anhydrous salt at  $20^\circ$ ), but undergoes considerable hydrolysis, unless excess of hydrochloric acid be present. Colloidal ferric hydroxide is formed in this way, and may be separated by dialysis (page 278).

The anhydrous salt boils at  $315^\circ$ , and at temperatures below  $400^\circ$  the vapour density corresponds with the formula  $\text{Fe}_2\text{Cl}_6$ ; from  $400^\circ$  to  $750^\circ$  the vapour density steadily diminishes to the value corresponding to  $\text{FeCl}_3$ . At still higher temperatures, a further slight fall in vapour density occurs; probably on account of dissociation into ferrous chloride and chlorine:



The elevation of the boiling point of ether or alcohol when ferric chloride is dissolved in them indicates a formula  $\text{FeCl}_3$ .

Ferric chloride solutions are yellow when hydrolysis does not occur (e.g., in ether or benzene) or has been prevented by addition of hydrochloric acid. Otherwise they are reddish on account of the formation of the hydroxide.

Ferric chloride forms a number of double salts which are garnet red crystalline substances, e.g.,  $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ ;  $(\text{NH}_4)_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ .

**Ferric nitrate**,  $\text{Fe}(\text{NO}_3)_3$ , can be made by treating iron with moderately dilute nitric acid (sp. gr. ca. 1.3). On addition of more concentrated nitric acid, almost colourless, but sometimes amethyst-coloured crystals of the composition  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  separate.

**Ferric sulphide**,  $\text{Fe}_2\text{S}_3$ , can be obtained by fusing equal weights of iron and sulphur at about  $550^\circ$ ; and by passing a current of hydrogen sulphide over warm ferric oxide, as in the purification of coal gas (page 382).

### Iron Disulphide, Iron Pyrites, $\text{FeS}_2$

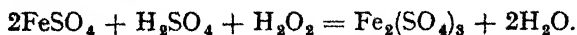
Although ferrous sulphide is rare in nature, iron pyrites is very common indeed. It occurs in two forms: one, *pyrite*, crystallizes in the cubic system and is very slowly oxidized in air; the other, *marcasite*, crystallizes in the rhombic system and oxidizes comparatively quickly. It is a hard yellow substance with an appearance resembling brass, and can be made artificially by heating iron with excess of sulphur at a low red heat,  $500^\circ$ .

When heated to  $700^\circ$ , it loses sulphur, and when heated in air it burns to ferric oxide and sulphur dioxide, and is extensively used as a

source of sulphur dioxide for sulphuric acid manufacture (see page 497). It is also used for making ferrous sulphate (page 921).

### Ferric Sulphate, $\text{Fe}_2(\text{SO}_4)_3$

This salt is prepared by adding sulphuric acid and an oxidizing agent, such as nitric acid or hydrogen peroxide, to ferrous sulphate solution and boiling the mixture until it ceases to give a blue precipitate with potassium ferricyanide:



After concentration, the solution deposits, when cooled, a whitish mass which has the composition  $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ . The anhydrous salt can be obtained by heating the hydrate.

Ferric sulphate, when heated, breaks up into ferric oxide and sulphur trioxide; this reaction was formerly made use of for the preparation of fuming, or Nordhausen sulphuric acid (page 509).

Ferric sulphate forms alums with the sulphates of the alkali metals, etc., the most important of which is **iron alum**,  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$   $24\text{H}_2\text{O}$ . This salt is used in analytical work as a standard of ferric iron as it is almost the only ferric salt which can be purified readily by crystallization.

## § 10 Ferrocyanides and Ferricyanides

Diesbach, a colour manufacturer of Berlin, accidentally discovered the colour now known as Prussian or Berlin blue, about 1704, and he mentioned the fact to the alchemist, Dippel, who investigated the subject, and according to Woodward (1724) prepared it by melting dried blood with potash salts and treating the aqueous extract of the mass with ferrous sulphate. J. Brown (1725) showed that animal flesh, and St. Geoffroy (1725) that other animal substances, could be used instead of blood. In 1752 Macquer noticed that when Prussian blue was boiled with an alkali, iron oxide separated from the solution and the mother-liquid contained a substance which separated in yellow crystals. It was then called *phlogisticated potash* and afterwards *prussiate of potash*, it is now known as *potassium ferrocyanide*. K. W. Scheele (1782-5) showed that when distilled with dilute acids, Prussian blue furnishes an acid which he named *prussic acid*. C. L. Berthollet (1787) showed that iron, as well as potash and prussic acid, is an essential constituent of the so-called prussiate of potash.

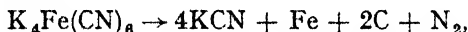
### Potassium Ferrocyanide, $\text{K}_4\text{Fe}(\text{C})\text{N}_6$

When nitrogenous refuse (blood, horns, leather scraps, etc.) is charred, and the black mass is ignited with potash and iron filings, something is formed which passes into solution when the mass is lixiviated with water. The aqueous solution on evaporation gives yellow crystals of potassium ferrocyanide with the empirical composition,  $\text{K}_4\text{FeC}_6\text{N}_6 \cdot 3\text{H}_2\text{O}$ . The same salt is obtained from the "spent

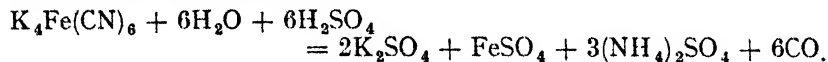
oxide" of the "purifiers" of gasworks which are used (q.v.) to remove the sulphur and cyanogen compounds from the gases formed during the distillation of coal. The "spent oxide" is boiled with lime. The soluble calcium ferrocyanide is leached from the mass, and converted into potassium salt by the treatment with potassium carbonate. The resulting potassium ferrocyanide is purified by crystallization. Sometimes the cyanogen compounds are removed from the coal gas before it reaches the purifiers by washing the gas in an alkaline solution with ferrous carbonate in suspension. **Sodium ferrocyanide**,  $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$ , is produced in an analogous way.

### Properties of Potassium Ferrocyanide

Potassium ferrocyanide crystallizes in laminated, sulphur-yellow crystals with three molecules of "water of crystallization,"  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ . The salt is soluble in water, but not in alcohol or ether. The aqueous solution has a bitter taste, but is not particularly poisonous. The salt loses its "water of crystallization" on warming, and the anhydrous salt remains behind as a white powder. The salt is decomposed when heated, forming potassium cyanide, KCN, and a mixture of carbon and iron possibly containing iron carbide, generally represented by the equation



although it is probably much more complicated than this. When warmed with *dilute* sulphuric acid, hydrogen cyanide (q.v.) is formed; with *concentrated* sulphuric acid, carbon monoxide is evolved:



This is, no doubt, a consequence of the hydrolysis of the hydrogen cyanide, first formed, to formic acid which is then dehydrated by the concentrated sulphuric acid (cf. page 398).

### Ferrocyanic Acid, $\text{H}_4\text{Fe}(\text{CN})_6$

When a saturated solution of potassium ferrocyanide, freed from dissolved air by boiling, is treated with concentrated hydrochloric acid in the cold, a white crystalline powder called ferrocyanic acid is formed; it has the empirical formula,  $\text{H}_4\text{Fe}(\text{CN})_6$ . Ferrocyanic acid turns blue on exposure to the air owing to partial decomposition and the formation of Prussian blue (q.v.) and when heated *in vacuo* at about  $300^\circ$  it furnishes a pale yellow powder with the empirical formula  $\text{Fe}(\text{CN})_2$ ; this powder is probably not a simple cyanide, but rather a ferrous ferrocyanide.

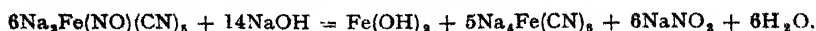
### Sodium Nitroprusside, $\text{Na}_2\text{Fe}(\text{NO})(\text{CN})_5 \cdot 2\text{H}_2\text{O}$

When, say, four grams of powdered potassium ferrocyanide are boiled for half an hour with 4 c.c. of concentrated nitric acid diluted with its own volume of

water, and the cold solution made alkaline with sodium hydroxide, ruby-red crystals of sodium nitroprusside are obtained. The sodium ferrocyanide is thought to be first oxidized to the ferricyanide, which reacts with NO:



Sodium nitroprusside is also formed on passing nitric oxide into acidified sodium ferrocyanide solution. When sodium nitroprusside is treated with alkalis, it furnishes sodium ferrocyanide, ferrous hydroxide, etc.:



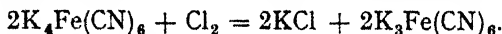
The salt is sometimes called *sodium nitroferrocyanide*. A solution of sodium nitroprusside is sometimes used as a test for sulphides since it gives a deep violet coloration with soluble sulphides.

The nitroprussides were formerly supposed to contain ferric iron, but Pauling (1931) and Sidgwick (1934) have suggested that the odd electron of the NO molecule enters the valency shell of the ferric ion forming a ferrous ion and that the : NO : radical thus left co-ordinates by means of the lone pair on the nitrogen. This view is supported by the fact that the nitroprusside is diamagnetic whereas potassium ferricyanide is paramagnetic.

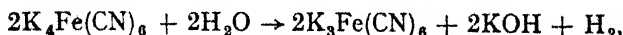
Nitroprussic acid,  $\text{H}_2\text{Fe}(\text{NO})(\text{CN})_5$ , has been obtained in dark-red monoclinic crystals by treating the silver salt with hydrochloric acid, or the barium salt with dilute sulphuric acid.

### Potassium Ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$

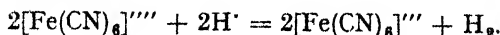
If an aqueous solution of potassium ferrocyanide be treated with oxidizing agents like chlorine, bromine, nitric acid, hydrogen peroxide, etc., it acquires a dark reddish colour, and crystals of potassium ferricyanide separate when the solution is concentrated by evaporation:



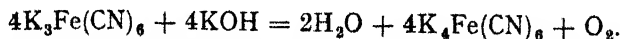
The potassium ferricyanide is separated from potassium chloride by re-crystallization. If an excess of chlorine be passed into a solution of potassium ferrocyanide, the solution deposits a greenish precipitate—called *Prussian green*. The oxidation of the ferrocyanide to ferricyanide is now conducted by the electrolysis of slightly alkaline solutions—hydrogen and potassium hydroxide are formed at the cathode:



or, in terms of ions:



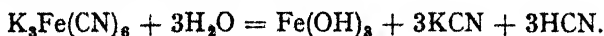
The ferricyanide is separated by crystallization. Potassium ferricyanide, also called *red prussiate of potash*, is a mild oxidizing agent in alkaline solutions, for it oxidizes "reducing agents" like sodium thiosulphate, hydrogen sulphide, etc., re-forming potassium ferrocyanide:



Thus, an aqueous solution of the ferricyanide is converted into ferrocyanide by potassium or sodium amalgam. Potassium ferricyanide



is rather more soluble in water than the ferrocyanide: thus, 100 grams of water at 0° dissolve 31 grams of potassium ferricyanide, and 13 grams of ferrocyanide; at 10° these numbers are respectively 36 and 20. Potassium ferricyanide is not soluble in alcohol. In neutral, aqueous, solution potassium ferricyanide undergoes slight hydrolysis; a change which is accelerated by light:



Hence the solution will not keep and should be freshly prepared before use. When a saturated solution of potassium ferricyanide is treated with concentrated hydrochloric acid, in the cold, reddish-brown, acicular crystals of tribasic **ferricyanic acid**,  $\text{H}_3\text{Fe}(\text{CN})_6$ , separate from the solution concentrated by evaporation *in vacuo*.

Various salts of ferrocyanic and ferricyanic acids have characteristic colours, as indicated in Table LXVIII, and consequently, potassium ferrocyanide and ferricyanide—particularly the former—are used in qualitative analysis.

TABLE LXVIII — PROPERTIES OF FERRO- AND FERRICYANIDES

	Ferrocyanides added to	Ferricyanides added to
Ferric chloride .	Deep blue precipitate of Prussian blue, insoluble in hydrochloric acid, soluble in oxalic acid.	No precipitate in neutral solutions, but the solution is coloured deep brown.
Ferrous chloride .	Bluish - white precipitate which rapidly darkens on exposure to air, or by adding a drop of bromine	Deep blue precipitate of Turnbull's blue.
Coppet sulphate .	Reddish-brown precipitate	Greenish-brown precipitate
Cobalt nitrate .	Greyish-green precipitate.	Red precipitate.
Silver nitrate .	White precipitate.	Red precipitate.

**Prussian blue**, or *Berlin blue*, is formed, as indicated in the preceding table, when excess of a solution of potassium ferrocyanide is added to a solution of a ferric salt. It is insoluble in hydrochloric acid, but soluble in oxalic acid, forming a deep blue solution. When heated with concentrated sulphuric acid Prussian blue yields hydrocyanic acid; and when boiled with alkaline hydroxides, ferric hydroxide is precipitated, and alkaline ferrocyanide remains in solution. Besides the "insoluble" Prussian blue, a *soluble or colloidal Prussian blue* is formed when rather less than an equivalent of a solution of a ferric salt is added to a solution of potassium ferrocyanide. By the addition of salt to the solution, the "soluble" Prussian blue is coagulated or "salted out," and the precipitate is then "insoluble" Prussian blue.

It is probable that these two "forms" of Prussian blue differ only in the size of the particles composing them.

When potassium ferricyanide solution is added to neutral or acid

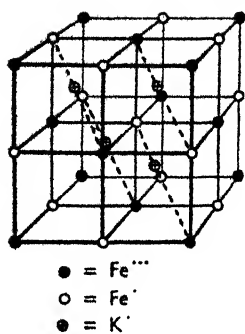


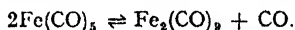
FIG. 39.7.  
Structure of Prussian  
(and Turnbull's) Blue

solutions of a ferrous salt, a dark blue precipitate called "Turnbull's blue" is formed.

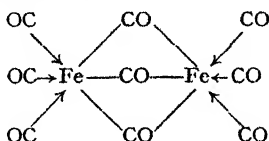
Prussian blue and Turnbull's blue should thus be ferric ferrocyanide and ferrous ferrocyanide respectively. It had long been suspected that they are not, in fact, distinct chemically and X-ray investigation has now shown (Keggin and Miles, 1936) that they are identical. The crystal lattice is cubic with alternate ferrous and ferric atoms at the corners of the cubes and with the CN radicals along the edges. The composition is now known to be  $\text{KFe}[\text{Fe}(\text{CN})_6]$  and the potassium atoms are situated at the centres of alternate cubes (see Fig. 39.7).

### § 11 Iron Carbonyls

Iron forms three compounds with carbon monoxide, known as carbonyls. If carbon monoxide be passed over finely divided iron at  $120^\circ$ , iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , is formed as a pale yellow viscous liquid. On exposure to light, it decomposes, forming iron enneacarbonyl,  $\text{Fe}_9(\text{CO})_9$ , and carbon monoxide. The enneacarbonyl decomposes when heated, forming carbon monoxide and the pentacarbonyl. If the enneacarbonyl be heated in an inert atmosphere, and in presence of an organic solvent, green crystals of a polymer of iron tetracarbonyl  $[\text{Fe}(\text{CO})_4]_n$ , are formed.



The structure of metallic carbonyls has been shown, by means of X-rays and electron diffraction, to involve co-ordination through the unshared pair of electrons on the carbon of the carbon monoxide. Iron pentacarbonyl thus has the form of a trigonal bipyramid in which all five carbon monoxide molecules are united to the iron by co-ordinate links, iron enneacarbonyl has six carbon monoxide molecules joined by co-ordinate links and three carbonyl groups joining the iron atoms by ordinary co-valencies, thus:



### § 12 Detection and Determination of Iron

Iron can be detected in compounds by fusion on charcoal with sodium carbonate, using a reducing flame, when the metal results and can be recognized by its magnetic properties. This reduction requires some care in its performance. Cobalt and nickel, if present, are formed similarly.

In solution, iron is detected by means of the reactions of ferrous and ferric salts with ferrocyanides, ferricyanides and thiocyanates (the latter give a blood-red coloration with ferric salts).

Iron is determined volumetrically when in the ferrous state by titration with potassium permanganate or dichromate. Ferric salts may be titrated with titanous chloride, or they may be reduced to the ferrous state and dealt with as before.

Gravimetrically, iron is determined by conversion first to the ferric state, by means of nitric acid; after which it is precipitated as hydroxide by ammonium hydroxide. The ferric hydroxide is filtered off, washed, dried, ignited and weighed as ferric oxide.

### {13 Cobalt, Co

#### History

The word "kobalt" occurs in the writings of B. Valentine and Paracelsus to denote a goblin supposed by the old Teutons and Scandinavians to haunt the mines, destroying the work of the miners, and giving them a lot of unnecessary trouble. The word is derived from the German *kobald*, an evil spirit. The church service in some mining districts once included a prayer that God would preserve the miners and their work from kobalds and other evil spirits. The term was applied to what were called "false ores," that is, ores which did not give metals when treated by the processes then in vogue for the extraction of the metals; and also to ores which had an objectionable smell. The term was gradually confined to the minerals used for colouring glass blue, and which are still used for making smalt. In 1735 Brandt stated that the blue colouring principle is due to the presence of a peculiar metal or semi-metal which he called "cobalt rex," hence our "cobalt." Brandt isolated the metal in 1742.

#### Occurrence

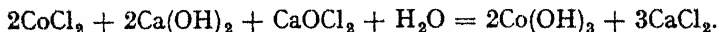
Cobalt is nearly always found in association with nickel, chiefly as arsenides, e.g., in *smaltite* or *cobalt speiss*,  $\text{CoAs}_2$ ; *cobaltite* or *cobalt glance*,  $\text{CoAsS}$ . The deposits near the town of Cobalt in the province of Ontario in Canada, where it occurs along with nickel and silver, were formerly the principal source of cobalt, but these are now showing signs of exhaustion and Northern Rhodesia and the Belgian Congo are becoming increasingly important as suppliers of cobalt ores.

#### Extraction

Cobalt ores are principally worked in order to get cobalt salts and not the metal. The ore is first roasted in a small blast furnace to remove arsenic as trioxide, which is condensed and used as a source of that element (page 834). The remainder of the ore forms a "speiss" of crude cobalt, nickel, etc., which is heated with common salt and then extracted with water. The insoluble residue is worked up for silver and the aqueous solution contains iron, cobalt, nickel and copper chlorides. The iron is removed by precipitation with limestone, copper

is removed from the filtrate by means of sodium carbonate and, finally, the cobalt is obtained as the oxide  $\text{Co}_2\text{O}_3$ .

Several methods are in use for separating cobalt and nickel; one of the most important being the Mond process for obtaining nickel by way of the carbonyl (page 935). Of other methods there may be mentioned the use of bleaching powder. The mixed oxides are dissolved in hydrochloric acid and the resulting solution neutralized with chalk. The clear solution is treated with bleaching powder which precipitates cobaltic hydroxide practically uncontaminated by nickel:



If the metal itself be required, it can be obtained by reducing the oxide in a current of hydrogen, by the aluminothermic method, or by electrolysis of cobalt ammonium sulphate solution.

### Properties

Cobalt is a white, malleable and ductile metal rather harder than iron. It is feebly magnetic, and melts at  $1492^\circ$ . When in bulk it is not attacked by air at ordinary temperatures, and only reacts slowly with oxygen at a red heat, but in the finely divided state it is sometimes pyrophoric. Dilute hydrochloric and sulphuric acids attack cobalt slowly and nitric acid dissolves it fairly readily.

### Uses

Cobalt has been used in electro-plating and has been suggested for use as a coinage metal. As a constituent of alloys it is beginning to be used more extensively. Some of these, e.g., stellite (page 867), and high-speed tool steels (page 880) have been mentioned already; in addition, reference may be made to *cochrome* (Co 60, Cr 14–16, Fe 24–26 per cent) which is similar to *nichrome* (page 867) and is used for similar purposes. *Alnico*, an alloy containing also nickel, copper and aluminium (Ni 18, Al 10, Co 12.5, Cu 6, Fe 53.5 per cent) has magnetic properties which make it outstanding for use in permanent magnets (e.g., for loudspeakers and magnetos).

Cobalt oxides and silicates are used for colouring glass, and pottery glazes. *Smalt*, much used for these purposes, is a potassium cobalt aluminosilicate. *Cobalt yellow* is a pigment which is a potassium cobaltinitrite. Cobalt salts of organic acids are used as driers in the manufacture of paints and varnishes.

### Atomic Weight

The specific heat of cobalt (0.103), and the position of the element in the Periodic System indicate a value for the atomic weight in the neighbourhood of 59. The most satisfactory method of determining an accurate value is by conversion of the chloride and bromide into the corresponding silver salts. As a result of the work of Baxter and

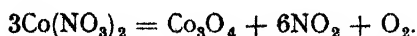
his collaborators, the International Committee has recommended the value 58.94.

### § 14 Oxides and Hydroxides of Cobalt

Cobalt forms four oxides, viz.,

Cobaltous oxide,  $\text{CoO}$ ;  
 Cobaltous oxide,  $\text{Co}_3\text{O}_4$ ;  
 Cobaltic oxide,  $\text{Co}_2\text{O}_3$ ;  
 Cobalt peroxide,  $\text{CoO}_2$ .

**Cobaltous oxide,  $\text{Co}_3\text{O}_4$ .** is obtained as a black powder by strongly heating cobalt nitrate:



It reacts with hydrochloric acid, chlorine being liberated, and a solution of cobalt chloride is formed.

#### **Cobaltic Oxide, $\text{Co}_2\text{O}_3$**

Cobaltic oxide is obtained by heating cobaltous nitrate or carbonate in air. It is a dark grey or brownish-black powder which forms an oxide corresponding with cobaltous,  $\text{Co}_3\text{O}_4$ , when heated to a point between the dissociation temperature  $373^\circ$  (760 mm.) and about  $700^\circ$ . **Cobaltic hydroxide,  $\text{Co}(\text{OH})_3$ ,** is formed as a black precipitate when a cobaltous salt is treated with alkaline hypochlorite. Both the oxide and the hydroxide dissolve in acids, forming brown solutions which contain unstable cobaltic salts; these salts decompose when warmed, forming cobaltous salts and oxygen or its equivalent. Hence cobaltic oxide behaves as a feebly basic oxide and as a polyoxide like nickelic oxide and manganese dioxide. (Cf. page 890.)

**Cobaltous oxide,  $\text{CoO}$ ,** is obtained by heating cobaltous hydroxide, carbonate or nitrate to  $1000^\circ$  in absence of air. It is a dark-brown or olive-green powder, which is stable in air, but when heated to between  $600^\circ$  and  $700^\circ$ , it absorbs oxygen and forms  $\text{Co}_3\text{O}_4$ . At still higher temperatures,  $\text{CoO}$  is re-formed. When heated in hydrogen or carbon monoxide, it is reduced to the metal. It reacts with acids forming cobaltous salts.

**Cobaltous hydroxide,  $\text{Co}(\text{OH})_2$ ,** is obtained when alkali hydroxides are added to solutions of cobaltous salts. It exists in two forms: a blue form, which is converted into a rose-pink form on boiling the suspension of the blue form in the solution from which it was precipitated. Both forms turn brown on exposure to the air because of the absorption of oxygen.

#### **Cobalt Peroxide, Cobalt Dioxide, $\text{CoO}_2$**

When a solution of cobalt sulphate is treated with iodine and sodium hydroxide a black precipitate results, believed to be cobalt dioxide.

If cobalt hydroxide be suspended in water and then treated with hydrogen peroxide, the resulting liquid, after filtration, is strongly acid and is believed to contain cobaltous acid,  $\text{H}_2\text{CoO}_4$ ; a green unstable solution of potassium cobaltite  $\text{K}_2\text{CoO}_4$ , is formed by the addition of potassium hydrogen carbonate to the solution of cobaltous acid.

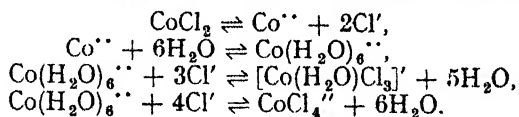
### § 15 Salts of Cobalt

In one sense cobalt gives rise to two series of salts derived respectively from cobaltous oxide and cobaltic oxide; but the latter are only stable in the form of complex compounds. The cobaltous salts are thus the ordinary salts of this element.

**Cobalt carbonate**,  $\text{CoCO}_3$ , is obtained as a bright red powder by addition of sodium bicarbonate solution, saturated with carbon dioxide, to a solution of a cobalt salt. If the reaction be carried out at a low temperature,  $\text{CoCO}_3 \cdot 6\text{H}_2\text{O}$  is formed; at a temperature of  $140^\circ$  the anhydrous salt results.

#### Cobalt Chloride, $\text{CoCl}_2$

The hydrated salt— $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ —crystallizes from solutions of the oxide or carbonate in hydrochloric acid in ruby-red monoclinic crystals, easily soluble in water (100 grams of water dissolve 32 grams of anhydrous salt at  $15^\circ$ ). The crystals at  $100^\circ$  form the monohydrate  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ ; and at about  $120^\circ$  the anhydrous chloride  $\text{CoCl}_2$ . The latter is deep blue but gives pink solutions when dissolved in cold water. The solution also changes colour when heated, becoming blue at about  $50^\circ$ . It is now thought that the pink solutions contain various hydrated ions such as  $\text{Co}(\text{H}_2\text{O})_6^{++}$ ; but that the blue solutions contain complex ions like  $\text{CoCl}_4^{--}$  or  $[\text{Co}(\text{H}_2\text{O})\text{Cl}_3]'$  (Bassett, 1930–34).



Solutions of cobalt chloride have been used for sympathetic ink. The pink solution is not visible when used for writing, but becomes blue when the paper bearing it is warmed. On cooling in moist air, the blue colour fades again.

#### Cobalt Nitrate, $\text{Co}(\text{NO}_3)_2$

The anhydrous salt is made by the action of nitrogen pentoxide, or a solution of nitrogen pentoxide in nitric acid, on the hydrated salt. It is a slightly pink powder which decomposes on heating with evolution of nitrous fumes.

Cobalt nitrate can be obtained in aqueous solution by dissolving the carbonate in dilute nitric acid. On evaporation, reddish crystals of the composition  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are obtained.

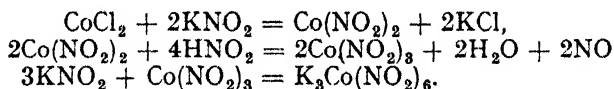
**Cobalt sulphide**,  $\text{CoS}$ , is formed as a black precipitate on addition of ammonium sulphide to a solution of a cobalt salt or on passing hydrogen sulphide through a solution of a cobalt salt containing ammonia and ammonium chloride. It is amorphous in appearance when first precipitated, and soluble in acids; on heating, it becomes insoluble and crystalline in character.

**Cobalt sulphate**,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ , is made by dissolving the monoxide or carbonate in dilute sulphuric acid. It crystallizes below  $40^\circ$  with 7 molecules of water forming rose-coloured crystals isomorphous with  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ .

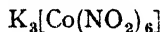
It readily forms a double salt with ammonium sulphate  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ , analogous to ferrous ammonium sulphate.

Simple **cobaltic salts** are unstable, but give rise to a number of stable complex compounds such as cobalt alums, cobaltcyanides, cobaltinitrites, and cobaltammines. The cobalt alums are isomorphous with other alums; an important one is **ammonium cobalt alum**,  $\text{NH}_4\text{Co}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , which is bright blue. Both cobalto- and cobaltcyanides are known, analogous to the ferro- and ferricyanides.

The cobaltinitrites are of some importance in analysis. If potassium nitrite be added to a solution of a cobaltous salt, acidified with acetic acid, a bright yellow crystalline precipitate of **potassium cobaltinitrite**,  $\text{K}_3\text{Co}(\text{NO}_2)_6 \cdot n\text{H}_2\text{O}$ , is formed. This substance is practically insoluble in water, whereas the corresponding sodium salt is soluble. Hence it is used as a reagent for testing (page 644) for the presence of potassium. Also nickel salts give a similar but *soluble* nickel nitrite and so the formation of the cobaltinitrite serves for the detection of cobalt in presence of nickel.



The probable formula for potassium cobaltinitrite is,



since it does not give the reactions of nitrites.

Cobaltammines are formed on addition of excess of ammonia to a solution of a cobalt salt; the mixture being then allowed to stand in contact with the air. They are discussed at the end of this chapter (page 946) along with other similar complex compounds.

#### Cobalt Carbonyls

Two cobalt carbonyls are known. By the action of carbon monoxide on cobalt at 30 atmospheres pressure and  $150^\circ$ , orange-red crystals of  $\text{Co}_2(\text{CO})_8$  are formed. These melt at  $51^\circ$  and at  $60^\circ$  decompose into black  $\text{Co}_4(\text{CO})_{12}$ .

### § 16 Detection and Determination of Cobalt

Cobalt is easily recognized by the blue colour of the borax bead which its compounds give when fused with borax on a platinum wire. In solution, the formation of potassium cobaltinitrite (described above) is a useful method of detection and of separation from nickel.

Cobalt is commonly determined by addition of potassium hypobromite solution to the solution of the cobalt salt whereby an indefinite mixture of hydroxides results. This is washed, dried and ignited,

giving a mixture of oxides, which are reduced to the metal in a current of hydrogen. If nickel be present, it is separated first by the cyanide process (page 938). Cobalt can be both detected and determined in presence of nickel by means of a solution of  $\alpha$ -nitroso- $\beta$ -naphthol in dilute acetic acid, which forms a dark red precipitate.

## § 17 Nickel, Ni

### History

Nickel seems to have been known to the Chinese in early times. In Europe, towards the end of the seventeenth century, the German term *kupfernickel* (false-copper) was applied to an ore which, while possessing the general appearance of a copper ore, yet gave no copper when treated by the general process then used for the extraction of copper. Nevertheless, the mineral was supposed to be an ore of copper, or a species of cobalt or arsenic united with copper. A. F. Cronstedt, 1751-54, stated that *kupfernickel* contains a metal which gives a brown, not a blue, colour with glass. Cronstedt's views were not accepted generally until T. Bergman had shown clearly that Cronstedt's metal was a new element in an impure condition. Bergman's arguments were mainly directed to controvert the view that nickel is a compound of cobalt, iron, arsenic, and copper, advocated by le Sage. He showed that nickel retains its individuality when arsenic is absent, and when no signs of cobalt or copper can be detected in solutions of the metal. Bergman also tried unsuccessfully to make nickel synthetically from mixtures of the elements in question.

### Occurrence

Cobalt and nickel are nearly always found associated with one another; both occur free in some meteorites. Nickel occurs as *kupfernickel* or *nicollite*,  $\text{NiAs}$ ; *mullerite*, or nickel blende,  $\text{NiS}$ ; *nickel glance*,  $\text{NiAsS}$ ; and *garnierite*, a silicate of magnesium and nickel  $(\text{NiMg})\text{H}_2\text{SiO}_4$ , found in New Caledonia. The most important ores come from Sudbury in Ontario.

### Extraction

The Sudbury ores contain chalcopyrite and other copper and iron minerals, as well as nickel; often these are embedded in other rocky materials. Preliminary concentration of the nickel ore is effected by flotation, and it is then roasted to remove some of the sulphur. The roasted ore is then smelted with quartz, coke, and limestone in a small blast furnace, when an impure mixture of nickel and copper sulphides and some iron remains. The product is then "blown" in a Bessemer type converter with a basic lining, to oxidize away the iron and most of the sulphur. There thus results a *matte* of nickel and copper, which can be used as it is for the manufacture of some alloys (e.g., monel



metal). To separate the copper the matte is melted with a mixture of sodium bisulphate (nitre cake) and coke in a vertical furnace (or cupola). Reduction of the sulphate to sulphide occurs and this dissolves cuprous sulphide in preference to nickel sulphide so that when the melt is run out and allowed to solidify two layers are formed. The upper one contains almost all the copper and a little nickel; the lower contains very little copper and the bulk of the nickel. The upper layer is returned to the cupola while the lower is first roasted to give the oxide which is then reduced to the crude metal for refining. (This is known as the Orford process.)

Two methods of refining are in use, viz., the electrolytic (or Canadian) process and the Mond (or Carbonyl) process. For the former process reduction of the crude oxide is effected by means of coal and the crude metal is melted and cast into anodes. The electrolyte used is nickel ammonium sulphate as in electroplating. In the Mond process the crude oxide is reduced by means of water gas at  $300^{\circ}$ , after which carbon monoxide is passed over the mixture of metals at  $50^{\circ}$ – $80^{\circ}$ . The nickel forms nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , which is volatile and is conveyed, along with excess carbon monoxide, to towers containing pellets of pure nickel at  $180^{\circ}$ . The carbonyl is decomposed into almost pure nickel, and carbon monoxide which is used again.

### Properties

Nickel is a moderately hard, white metal, which melts at  $1453^{\circ}$ , and is magnetic. It is stable in air at ordinary temperatures, and burns in oxygen forming nickelous oxide  $\text{NiO}$ . It is not affected by water, but decomposes steam at a red heat; it is only slowly acted upon by dilute hydrochloric and sulphuric acids; but nitric acid attacks nickel readily, forming nickel nitrate.

### Alloys and Uses

Nickel is much used for "nickel plating" other metals on account of its silvery appearance, and the fact that it does not readily tarnish in air. The nickel is deposited from a double sulphate of ammonium and nickel by a process similar to that used for "silver or gold plating." Nickel is used in making several important alloys, being probably the most versatile metal for this purpose. *Nickel steel*, containing 2 to 5 per cent of nickel, is used for case-hardening (page 915), and nickel-chrome steels with 1.5 to 3 per cent of nickel and 0.5 to 1.2 per cent of chromium are exceedingly tough and shock-resisting and are used for the crankshafts of internal combustion engines, gears and similar purposes. With higher percentages of nickel and chromium (6 to 12 per cent of nickel, 16 to 18 per cent of chromium) stainless steels result; with higher percentages still of alloying metals heat-resisting alloys are formed. (Compare nichrome, page 867.) *Invar*, an alloy of nickel and iron containing 35 per cent of nickel, has a coefficient of expansion of

almost zero; *permalloy* (21.5 per cent of nickel and 78.5 per cent of iron) has unusual magnetic properties (low hysteresis and high permeability in weak fields) which make it important for high-speed telephony and telegraphy. *Platinite* is an alloy of 60 per cent of iron with 40 per cent of nickel which expands at the same rate as glass and so is used in the manufacture of electric lamps.

When nickel is added to brass a series of *nickel-silvers* results which are used as the basis (untarnishable) for plated silverware. An alloy of 70 per cent of nickel and 30 per cent of copper is known as *Monel metal*. It is very resistant to corrosion and is used in chemical industry and for domestic purposes. *Cupronickel* (copper 75 per cent, nickel 25 per cent) is now the standard alloy for British (so-called) silver coinage. *Manganin* is an alloy of nickel with copper and manganese which is used for electrical resistance coils since its specific resistance is high and the temperature coefficient of resistance very low.

Finely divided nickel is used as a catalyst in many hydrogenation reactions; for example in the "hardening" of vegetable and other oils for the manufacture of margarine.

### Atomic Weight

The atomic weight of nickel has been determined in a manner similar to that of cobalt. The International Committee recommends, at present, the value 58.71, based on the work of Richards and of Baxter and their collaborators and on more recent determinations of the mass numbers and abundance ratios of the isotopes.

## § 18 Oxides and Hydroxides of Nickel

A number of oxides of nickel has been reported, but only two seem to be unquestioned, viz.,

Nickelous oxide,  $\text{NiO}$ ;

Nickel dioxide,  $\text{NiO}_2$ .

In addition to these, a sesquioxide,  $\text{Ni}_2\text{O}_3$ , nickelous oxide,  $\text{Ni}_3\text{O}_4$ , and a peroxide,  $\text{NiO}_4$ , have been reported.

**Nickelous oxide**,  $\text{NiO}$ , is obtained as a greenish powder when the hydroxide or carbonate is heated out of contact with the air. On heating, it is said to form the sesquioxide, and it reacts with acids forming nickelous salts.

### Nickelous Hydroxide, $\text{Ni}(\text{OH})_2$

When potassium hydroxide is added to a solution of a nickel salt, a pale green precipitate of nickelous hydroxide separates. Unlike ferrous and cobaltous hydroxides, this precipitate does not oxidize on exposure to the air. It dissolves in ammonia and ammonium salts, forming ammines, and unlike the corresponding cobalt solution does not absorb oxygen from the air. It reacts with acids forming nickelous salts.

**Nickel Dioxide,  $\text{NiO}_2$** 

Two probably isomeric nickel dioxides have been reported—a black dioxide is made by the action of bromine, or hypochlorites or hypobromites on nickelous hydroxide; and a green one by the action of hydrogen peroxide on nickelous chloride in the cold, followed by treatment with alcoholic potash. The green oxide is remarkably like hydrogen peroxide in its chemical properties, and is different from the black oxide. Hence it has been suggested that the green oxide is a peroxide or super oxide with nickel bivalent; and the black oxide is a dioxide or polyoxide, nickel quadrivalent.

The formation and decomposition of an oxide of nickel containing more oxygen than nickelous oxide (which may be  $\text{Ni}_2\text{O}_3$  or  $\text{NiO}_2$ ) is the basis of the Edison nickel-iron accumulator just as lead dioxide is the basis of the action of the lead accumulator (page 796).

If nickel oxide be heated with barium carbonate in an electric furnace, a dark-coloured crystalline mass of **barium nickelite**,  $\text{BaO} \cdot 2\text{NiO}_2$ , is formed. Barium nickelite is decomposed by water.

**Nickelic oxide**,  $\text{Ni}_2\text{O}_3$ , is said to be formed as a black powder when nickelous oxide is heated in air, and when the nitrate or carbonate is ignited in air at a low temperature, but it is thought to be actually a mixture of  $\text{NiO}_2$  and  $\text{NiO}$ .

**Nickelic hydroxide**,  $\text{Ni}(\text{OH})_3$ , is precipitated when chlorine is passed through water or alkali hydroxide solution in which nickelous oxide is suspended, or when a nickel salt is treated with a solution of bleaching powder. The oxide (if it exists) and hydroxide do not appear to be basic, for when treated with acids nickelous salts and oxygen result.

**Nickelous oxide**,  $\text{Ni}_3\text{O}_4$ , is reported to be formed when moist oxygen is passed over nickel chloride at  $400^\circ$ . There are doubts about its existence: it is thought by some to be a mixture of  $\text{NiO}$  and  $\text{NiO}_2$ .

**§ 19 Salts of Nickel**

Nickel forms only one stable series of salts, although, as with cobalt, some complex nickelic derivatives are known.

**Nickel carbonate**,  $\text{NiCO}_3$ , is obtained in green crystals by adding nickel sulphate to a solution of sodium bicarbonate saturated with carbon dioxide. The addition of sodium carbonate to solutions of nickel salts precipitates basic nickel carbonates.

**Nickel chloride**,  $\text{NiCl}_2$ , is obtained in solution by the action of dilute hydrochloric acid on the oxide or carbonate. It crystallizes from this solution in green crystals of the composition,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , which effloresce slightly in air. On heating, the anhydrous salt can be obtained; it is also formed by the action of chlorine on finely divided nickel. It is a golden-yellow solid, which combines with ammonia.

**Nickel Nitrate,  $\text{Ni}(\text{NO}_3)_2$** 

Nickel dissolves readily in dilute nitric acid, and on evaporation, the solution deposits green monoclinic crystals of the composition  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . These are very soluble in water. On heating, some of the water of crystallization is driven off, but the nitrate decomposes

before it has become anhydrous, yielding nickelous oxide, nitrogen peroxide and oxygen:



**Nickel sulphide**,  $\text{NiS}$ , is formed as a black precipitate when ammonium sulphide is added to a solution of a nickel salt, or by passing hydrogen sulphide through a nickel salt solution containing also ammonia and ammonium chloride. As thus precipitated, it is soluble in acids, but on standing, or on boiling, it is quickly converted into a form which is insoluble in acids. It thus resembles cobalt sulphide in that neither sulphide is precipitated by hydrogen sulphide in acid solution; yet, as obtained by precipitation in alkaline solution, it is insoluble in acids, after quite a short time. It is supposed to exist in three forms (Thiel and Gessner, 1914).

### Nickel Sulphate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

By adding nickelous oxide or carbonate to dilute sulphuric acid and evaporating the resulting solution, green crystals of nickel sulphate heptahydrate separate, which are isomorphous with the corresponding hydrates of ferrous sulphate, magnesium sulphate, etc. It is the best known of the nickel salts, and is readily soluble in water. It combines with ammonia gas forming an unstable, dark blue compound analogous to the corresponding compound of copper sulphate. It also forms a stable double compound with ammonium sulphate, **nickel ammonium sulphate**,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , analogous to ferrous ammonium sulphate, which is used extensively in nickel-plating.

**Nickel carbonyl**,  $\text{Ni}(\text{CO})_4$ , is a colourless liquid, obtained by passing carbon monoxide over reduced nickel at  $50^\circ\text{--}80^\circ$ . It boils at  $43^\circ$ , and on heating decomposes into nickel and carbon monoxide. It is used industrially for the purification of nickel by the Mond process (page 935).

## § 20 Detection and Determination of Nickel

Nickel salts give green solutions, black sulphide precipitates with hydrogen sulphide in alkaline solution, and with ammonium hydroxide a pale green precipitate, soluble in excess to give a blue solution. When cobalt is also present, the nickel may be detected by adding excess of potassium cyanide to the solution until the precipitates first formed re-dissolve, owing to the formation of cobalto- and nickelocyanides. On boiling the solution, the cobaltocyanide is oxidized to the cobaltcyanide, and if sodium hypochlorite or hypobromite solution be now added, hydrated nickel dioxide is obtained as a black precipitate, while the cobalt remains in solution.

Alternatively, dimethyl glyoxime (which is also used for the quantitative determination of nickel) may be employed. In neutral or alkaline solution this reagent precipitates nickel quantitatively as a scarlet solid, but does not precipitate cobalt. This affords a very

delicate test for nickel, and for the estimation, the precipitate can be dried at  $110^{\circ}$  and weighed as such— $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$ —or ignited and weighed as the oxide,  $\text{NiO}$ .

### § 21 The Platinum Metals

The "platinum metals" are the two heaviest triads of the eighth group, and thus include ruthenium, Ru; rhodium, Rh; and palladium, Pd; and osmium, Os; iridium, Ir; and platinum, Pt, itself. They occur together and have many properties in common (see below).

#### History

There is supposed to be a reference to platinum in Pliny's *Natural History* under the name "aluta." The term "platina del Pinto," for a white metal resembling silver, has been for a long time in general use by the Spaniards in South America. "Platina" is the diminutive form of the Spanish *plata*, silver, and "Pinto" has reference to the river where it was discovered. At one time its export from South America was forbidden by the Spanish Government, who ordered it to be thrown into the sea to prevent its being used for adulterating gold. In 1788, the Spanish Government bought it for about 8s. per lb., presumably for adulterating gold. It was brought to Europe in 1735 by C. Wood, and W. Brownrigg and R. Watson described its properties in 1750. The platina del Pinto of Choca (Colombia) attracted the attention of Antonio de Ulloa in 1748; J. J. Scaliger of Leyden, 1558, also referred to an infusible metal which has been taken to have been platinum. The metal attracted much attention at the time. Before 1823, most of the platinum in commerce came from South America. Platinum was discovered in the Urals in 1819, and in 1824 Russia began exporting platinum; since that time and until the Russian revolution most of the platinum of commerce came from that source. Now a large proportion of the world production comes from South Africa.

Osmium and iridium were discovered by S. Tennant, 1802 to 1803; rhodium and palladium by W. H. Wollaston, 1803 to 1804; and ruthenium by K. Claus in 1845. All these metals were found during the study of native platinum. "Osmium" is named from the Greek *ὀσμή* (*osme*), a smell; "iridium" is named from the Greek *ἴρις* (*iris*), a rainbow, from the varying tint of its salts; "rhodium" is named from the Greek *ῥόδον* (*rhodon*), a rose, from the rose-red colour of its salts; "palladium" is named after the planet Pallas, which was discovered in the same year, 1802, as palladium was announced by Wollaston; "ruthenium" is named after *ruthen*, for Russia.

#### Occurrence

Platinum and the platinum metals occur native in three groups of mountain ranges, viz., those which run from Alaska to Peru; the Urals, Abyssinia and Rhodesia; and in East Australia, the East Indies

and Japan. Relatively large quantities are found associated with the nickel ores at Sudbury (Ontario).

In 1919 the total world production of platinum was  $6\frac{1}{2}$  tons; in 1939 it was about  $12\frac{1}{2}$  tons, of which over 40 per cent came from Sudbury. Before the Russian revolution practically all the platinum of commerce came from the Ural mountains (95 per cent), and when this source dried up (so far as the rest of the world was concerned) the price of platinum rose to 770s. per ounce. In 1924 production from the Sudbury ores and South Africa began, and by 1931 the price was down to 97s. per ounce. It is now (1960) about 600s.

### Extraction of the Metals

Half of the output of platinum and platinum metals of the Western world is now derived from South African deposits and is refined in England. These deposits consist largely of copper and nickel compounds associated with the platinum metals. The ores are smelted somewhat as described under the Orford process for nickel (page 934) whereby a *matte* results which separates into two layers, an upper layer of copper and a lower layer of nickel. The platinum metals are concentrated mainly in the lower layer but a significant amount remains in the upper layer along with any gold present. They are recovered in the anode slimes resulting from electrolysis using the crude metals obtained from these products as anodes. The copper and nickel are valuable by-products.

Gold can be removed from platinum concentrates by the amalgamation process. About 1860, the platinum, contaminated more or less with other metals, was extracted by a smelting process; today, a wet process is used. Details of the process are a "trade secret." In a general way it may be said that the concentrates are digested with dilute aqua regia under pressure. The insoluble residue contains osmiridium, an alloy containing mainly iridium and osmium but also some platinum, ruthenium and rhodium. Osmium and ruthenium form volatile oxygen compounds which can be easily removed from the solution by distillation. The solution of crude platinum in aqua regia is evaporated to dryness and heated to  $125^{\circ}$ ; the residue is then dissolved in water; acidified with hydrochloric acid; and treated with ammonium chloride, when a precipitate containing platinum and iridium compounds is obtained from which the metals are obtained by ignition. Aqua regia dissolves the residual platinum, not iridium. The platinum can be obtained by precipitation as before. The mother liquid is worked over for palladium and rhodium. The further separation of the platinum metals from one another is a difficult and laborious operation because the properties of the metals are so much alike; and because the behaviour of the salts of one element is modified by the presence of others. Thus, iridium does not dissolve in aqua regia, but if iridium be alloyed with platinum, some iridium passes into solution when the alloy is digested in aqua regia.

## § 22 Properties and Uses of the Platinum Metals

The metals are greyish-white and lustrous. They all melt at a high temperature. They are not acted upon by air or oxygen at ordinary temperatures. Osmium alone burns when strongly heated in air forming the tetroxide  $\text{OsO}_4$ ; the others are scarcely affected, chemically, at any temperature. Palladium readily dissolves in hot nitric acid and very sparingly in hydrochloric acid, but the other metals are scarcely affected by hot acids. Aqua regia attacks osmium, forming osmium tetroxide,  $\text{OsO}_4$ ; and it dissolves platinum forming the tetrachloride,  $\text{PtCl}_4$ ; ruthenium is slowly dissolved, while iridium and rhodium are not appreciably attacked, unless in a very finely divided condition. The native platinum alloy stubbornly resists attack by chemical reagents—even aqua regia. The metals are readily reduced from their compounds, which fact probably accounts for their occurrence free in nature. The metals fall naturally into two groups with nearly equal atomic weights. The *light platinum metals* include ruthenium, rhodium, and palladium; the *heavy platinum metals* include osmium, iridium, and platinum. Palladium is related to silver, and platinum to gold, as indicated in Table LXIX.

TABLE LXIX.—PROPERTIES OF THE PLATINUM METALS

	Light				Heavy			
	Ru	Rh	Pd	Ag	Os	Ir	Pt	Au
Atomic weight	101.1	102.91	106.4	107.88	190.2	192.2	195.09	197.0
Specific gravity	12.25	12.41	12	10.5	22.48	22.4	21.45	19.3
Atomic volume	8.3	8.5	8.9	10.2	8.5	8.6	9.1	10.2
Melting point	2450°	1960°	1552°	961°	2700°	2443°	1769°	1063°
Boiling point	4110°	3960°	3560°	2193°	4400°	4350°	4000°	2660°
Valency	2, 3, 4, 6, 7, 8	2, 3, 4	2, 4	1, 2	2, 3, 4, 8	1, 2, 3, 4, 6	2, 3, 4	1, 3

Platinum is a greyish-white metal with a brilliant lustre. It is harder than copper, silver or gold. It is ductile and malleable, and usually comes on the market in the form of foil or wire. Platinum has also the valuable quality that it softens like iron before melting, so that like iron it can be welded. Platinum melts at 1769°, and boils at about 4000°. Platinum and rhodium do not volatilize appreciably at 900°, but at 1300° volatilization can be detected. Appreciable quantities of the metals palladium, iridium, and ruthenium volatilize at 900°, and at 1300° the effect is very marked. Iridium is readily oxidized to a volatile sesquioxide when heated just below 1000°; but it is doubtful if platinum is oxidized below 1300°. Molten platinum, rhodium and ruthenium, like molten silver, absorb oxygen which is given off as the molten metal cools, hence it is liable to "spitting." Platinum is not attacked by pure hydrofluoric, hydrochloric, nitric

and sulphuric acids. It is readily dissolved by aqua regia and by solutions containing chlorine: cf. gold. When platinum is alloyed with silver, copper, lead, zinc, etc., it is attacked and partly dissolved by nitric acid, probably forming a **platinum nitrate**.

The high fusing temperature, and the fact that platinum is not attacked by air and strong acids, enable it to be used in the manufacture of apparatus—dishes, crucibles, stills, etc.—for many chemical operations which could not be readily performed with apparatus made from other available materials. The analysis of many minerals could not be so readily conducted as at present if it were not for the valuable qualities of platinum.

Platinum is attacked by alkalis, nitrates, cyanides, and phosphates under reducing conditions. With phosphorus it forms **platinum phosphide**; with sulphur, **platinum sulphide**,  $\text{PtS}$ ; with sulphur and dry alkali **platinum disulphide**,  $\text{PtS}_2$ ; with arsenic, **platinum arsenide**,  $\text{Pt}_2\text{As}_3$ . An arsenide called *sperrylite*,  $\text{PtAs}_2$ , associated with nickel sulphide occurs at Sudbury (Ontario). Platinum also alloys directly with metals like lead, silver, zinc, etc., but not mercury. Hence platinum crucibles must not be heated with these metals. Carbon alloys with platinum forming a brittle **platinum carbide**, and hence platinum crucibles must not be heated in a smoky flame.

Platinum has nearly the same coefficient of expansion as glass, and platinum wires can be fused in glass so as to make gas-tight joints. Platinum is also a good conductor of electricity, and large quantities were formerly used in electric light bulbs, short pieces of platinum wire being fused into the glass at the base of the bulb, and connected with the filament inside. Manganin, or copper coated with boron trioxide, or *kovar* (an alloy of iron, cobalt, nickel and manganese) are now used instead. Platinum is used in jewellery, in making scientific and surgical instruments, as a catalyst (cf. pages 448 and 501) and for contacts in electrical apparatus.

Platinum-iridium alloys are hard and elastic; malleable and ductile; and less fusible than platinum. If more than 20 per cent of iridium be present, the alloys are exceedingly difficult to work. An alloy of 10 per cent iridium and 90 per cent platinum was chosen by the International Committee on Weights and Measures for preserving the standards of length and weight. Platinum-iridium wire with platinum wire is used as a thermocouple for temperatures up to  $1000^\circ$ ; and platinum-rhodium wires are used with platinum in a similar way for temperatures up to  $1400^\circ$ . Commercial platinum has 2 per cent of iridium, and it appears to lose this constituent gradually when heated to a high temperature. The result is that platinum crucibles made from commercial platinum lose in weight every time they are heated for some time in the gas blowpipe. This is a source of annoyance. The high fusing temperature of osmium led to its use for a short time (usually in the form of an alloy with tungsten) for the manufacture of filaments for incandescent electric lamps, but, on account of the scarcity and



high cost of osmium it was soon given up and tungsten is now always used by itself. Iridium is very hard and so is used for tipping gold nibs. It has advantages over platinum for use in crucibles since it does not suffer attack when heated with carbon, phosphorus or aqua regia. The standard metre in Paris is made of an alloy of 90 per cent of platinum and 10 per cent of iridium. Palladium is used for absorbing hydrogen and for the detection of carbon monoxide (page 404). Osmium tetroxide is used for staining and hardening organic tissues in histology. It is also a valuable catalyst in organic chemistry.

Rhodium is the most expensive of all metals used as such. In the form of an alloy with platinum it is used for laboratory apparatus and for the heating wire of laboratory electric furnaces. One of its most recent uses is for plating on silverware since a layer 0.00002 inch thick is amply sufficient to prevent tarnishing completely and its "reflectivity" is the highest of all metals. Ruthenium is used for alloying with platinum for use in thermocouples and with platinum or palladium for use in jewellery. Palladium is also extremely malleable and is used in the form of palladium-leaf (cf. gold-leaf) for protection against corrosion and for decoration.

When platinum is precipitated from solutions of the tetrachloride by reducing agents, a velvet black powder called **platinum black** is obtained; when ammonium chloroplatinate is calcined, the metal remains behind as a spongy mass called **spongy platinum**; and if asbestos be soaked in a solution of platinum chloride and ignited, the asbestos permeated with platinum is called **platinized asbestos**. Platinum sponge, platinum black, and platinized asbestos adsorb large quantities of oxygen gas, and they can then be used as oxidizing agents. Platinum black can adsorb 100 times its volume of oxygen and 110 times its volume of hydrogen. Palladium black adsorbs about 900 times its volume of hydrogen. This property of occluding gases is shown in a less marked degree by iron, nickel and cobalt, as well as by copper, gold and silver. Spongy platinum will cause a mixture of hydrogen and oxygen to unite with explosion; spongy palladium without explosion. A jet of hydrogen directed on to finely divided platinum will cause the platinum to glow and finally ignite the jet of gas. Alcohol dropped on to iridium black takes fire. Similarly coal gas can be ignited by spongy platinum, and this property was utilized in making the so-called "self-lighting Bunsen burners." The catalytic properties of platinum metals are used in industry for promoting chemical changes, e.g., the oxidation of ammonia for the manufacture of nitric acid and the contact process for sulphuric acid.

### § 23 Oxides and Hydroxides of the Platinum Metals

When a solution of potassium chloroplatinite or of platinum chloride is treated with an alkaline hydroxide, **platinous hydroxide**,  $\text{Pt}(\text{OH})_4$ , is precipitated as a black powder. It is soluble in the haloid acids—hydrochloric and hydrobromic acids—and in sulphurous acid, but not in the other oxy-acids, and thus forms

the corresponding platinous salts. The hydroxide is decomposed into the metal and platinum dioxide,  $\text{PtO}_2$ , by boiling alkaline hydroxides:



When gently ignited, platinous hydroxide forms the corresponding **platinous oxide**,  $\text{PtO}$ , as a dark powder insoluble in water and in most acids. It is doubtful if  $\text{IrO}$  has been made. Palladium black warmed in air furnishes a dark bluish-green **palladous oxide**,  $\text{PdO}$ , which decomposes into the metal and oxygen at a higher temperature.

When a boiling solution of potassium hydroxide is added to a solution of platinum tetrachloride, and the precipitated **platinic hydroxide**,  $\text{Pt}(\text{OH})_4$ , is washed with acetic acid to remove the potash, a yellowish powder is obtained which dissolves in acids, forming **platinic salts**, and in bases forming a series of salts called the **platinates**. For instance, with sodium hydroxide, yellow crystals of **sodium platinate**,  $\text{Na}_2\text{O} \cdot 3\text{PtO}_2 \cdot 6\text{H}_2\text{O}$ , are obtained. Hence platinic hydroxide is an acidic and a basic compound. Platinic hydroxide,  $\text{Pt}(\text{OH})_4$ , is a type of similar compounds formed by the whole six of the platinum metals. The hydroxides when heated form dark grey powders of the dioxide—e.g.,  $\text{PtO}_2$ ,  $\text{IrO}_2$ , etc.

Ruthenium, osmium, iridium, and rhodium form **sesquioxides**:  $\text{Ru}_2\text{O}_3$ ;  $\text{Os}_2\text{O}_3$ ;  $\text{Ir}_2\text{O}_3$ ;  $\text{Rh}_2\text{O}_3$ . Ruthenium and osmium form compounds corresponding with the **trioxides**,  $\text{RuO}_3$  and  $\text{OsO}_3$ . A more or less impure  $\text{IrO}_3$  has been made. Thus, **potassium ruthenate**,  $\text{K}_2\text{RuO}_4$ ; and **potassium perruthenate**,  $\text{KRuO}_4$ , call to mind potassium manganate and permanganate. Ruthenium and osmium also form **tetroxides** of the type  $\text{RuO}_4$  and  $\text{OsO}_4$  respectively. These compounds represent the highest known state of oxidation of any single metal. The nearest approach to this state of oxidation occurs with perchloric and permanganic acids. The tetroxides dissolve in water but the solutions are not acid: (1) they are neutral to litmus; (2) do not decompose carbonates; and (3) form crystalline salts. The acids show no signs of hydrolysis. The term "osmic acid" for osmium tetroxide is thus a misnomer. Both tetroxides,  $\text{RuO}_4$  and  $\text{OsO}_4$ , melt at a low temperature, about  $+40^\circ$ , and boil at about  $100^\circ$  giving irritating vapours. Osmium tetroxide vapours are very poisonous, and seriously injure the eyes. They decompose on further heating into the dioxide and oxygen. The solutions are reduced by organic matters and the finely divided metal is precipitated: a 1 per cent solution is therefore used in microscopy for staining fat globules. The doubt whether, say, osmium is really octovalent in the tetroxide was lessened when osmium octofluoride,  $\text{OsF}_8$ , was obtained with a vapour density of 355—theoretically 343 for  $\text{OsF}_8$ —by the action of fluorine on osmium. *En passant*, it may be added that osmium tetrafluoride,  $\text{OsF}_4$ , and osmium hexafluoride,  $\text{OsF}_6$ , are formed at the same time. The tetrafluoride predominates when the action occurs at about  $100^\circ$ , and the other two fluorides, when the action occurs at about  $250^\circ$ . The octofluoride is separated in lemon-yellow crystals, melting at  $34.5^\circ$ , by cooling the product *in vacuo* in liquid air.

## § 24 Other Compounds of the Platinum Metals

### Platinum Fluorides

The existence of **platinum tetrafluoride**  $\text{PtF}_4$ , was established (by Sharpe) in 1950; a hexafluoride ( $\text{PtCl}_6$ ) was reported by Neinstock (1956); a **pentafluoride** ( $\text{PtF}_5$ ) and an **oxyfluoride** ( $\text{PtOF}_4$ ) have been described recently (Bartlett and Lohman, 1960).

### Platinum Tetrachloride, $\text{PtCl}_4$

Platinum dissolves in aqua regia. If the solution of hydrochloro-platinic acid,  $\text{H}_2\text{PtCl}_6$ , be evaporated to dryness, and the residue gently

heated, a solution of the residue in hot water deposits reddish-brown crystals of  $\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$  on cooling. The anhydrous chloride,  $\text{PtCl}_4$ , can be made by drying the crystals over sulphuric acid and warming them in a current of chlorine; or by heating hydrochloroplatinic acid in a current of hydrogen chloride between  $165^\circ$  and  $200^\circ$ .

If a stream of chlorine be passed over hydrochloroplatinic acid between  $364^\circ$  and  $374^\circ$ , the tetrachloride is formed; between  $430^\circ$  and  $440^\circ$  what appears to be the trichloride,  $\text{PtCl}_3$ ; about  $582^\circ$ , platinum dichloride appears, and it has been reported that at the same temperature some monochloride is formed, but this lacks confirmation. Iridium chlorides,  $\text{IrCl}_4$ ,  $\text{IrCl}_3$ ,  $\text{IrCl}_2$ , and  $\text{IrCl}$ , have been reported to be formed under similar circumstances respectively at  $100^\circ$ ,  $763^\circ$ ,  $773^\circ$ , and  $798^\circ$ . Chlorides of all six platinum metals of the type  $\text{PtCl}_4$  are known. **Palladium tetrachloride** is not known in a free state, but double chlorides with potassium, etc., are known.

### Chloroplatinates

If platinum chloride be crystallized from a solution acidified with hydrochloric acid, or if an aqua regia solution of the metal be evaporated a number of times with an excess of hydrochloric acid to drive off the nitric acid, reddish-brown deliquescent crystals of the complex acid,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  are formed. This substance—the “platinum chloride” of commerce—is really **hydrochloroplatinic acid**. The acid is dibasic, and it forms a characteristic series of complex salts—the chloroplatinates. **Potassium chloroplatinate**,  $\text{K}_2\text{PtCl}_6$ , for example, is a yellow crystalline precipitate made by adding the acid to a solution of potassium chloride. While the solubilities of the normal alkali chlorides in water *increase* in passing from lithium to caesium, the chloroplatinates *decrease* in solubility in passing from lithium to caesium. For instance, 100 c.c. of water at  $10^\circ$  dissolves, in grams:

$\text{Li}_2\text{PtCl}_6$	$\text{Na}_2\text{PtCl}_6$	$\text{K}_2\text{PtCl}_6$	$\text{Rb}_2\text{PtCl}_6$	$\text{Cs}_2\text{PtCl}_6$
Very soluble	1.15	0.90	0.15	0.05

The solubility of **ammonium chloroplatinate**,  $(\text{NH}_4)_2\text{PtCl}_6$ , is 0.6 at  $10^\circ$ , and it thus comes between potassium and rubidium chloroplatinates. The fact that the sodium salt is fairly soluble in 80 per cent alcohol, while the potassium salt is almost insoluble, enables a mixture of the chloroplatinates of sodium and potassium to be separated. The ammonium salt behaves like the potassium salt. During the electrolysis of ordinary salts—silver nitrate, potassium chloride, etc.—the metal is deposited on the cathode; with the chloroplatinates, some of the platinum migrates as a  $\text{PtCl}_6^{--}$ -ion to the anode compartment. Again, silver nitrate precipitates  $\text{Ag}_2\text{PtCl}_6$ , not  $\text{AgCl}$ , thus confirming the deduction that “ $\text{PtCl}_6$ ” is a bivalent complex acid radical or that the solution of the acid furnishes the ions  $2\text{H}^+$  and  $\text{PtCl}_6^{--}$  in solution. The constitution of the chloroplatinates will be discussed later.

**Platinum Dichloride,  $\text{PtCl}_2$** 

If hydrochloroplatinic acid be heated between  $250^\circ$  and  $300^\circ$ , it furnishes a grey granular powder of platinum dichloride,  $\text{PtCl}_2$ , insoluble in water; at higher temperatures, it decomposes into platinum and chlorine. Platinum dichloride is also formed when platinum is heated to about  $582^\circ$  in chlorine gas. All six metals of the platinum series form salts of the type  $\text{PtCl}_2$ . Dihydrated **palladium dichloride**,  $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ , is obtained by the simultaneous action of hydrochloric acid and chlorine, or a little nitric acid, upon palladium. The solution deposits brownish-red crystals of the dihydrate on evaporation under reduced pressure. The anhydrous salt is formed if the crystals are warmed; and also by the action of chlorine on the warm sulphide. The garnet-red crystals of the anhydrous salt decompose at a red heat, forming what has been reported as monochloride,  $\text{PdCl}$ , but this is not certain. **Palladous iodide**,  $\text{PdI}_2$ , is precipitated as a black insoluble powder when potassium iodide is added to solutions of palladous chloride. This reaction is used sometimes for the separation of iodine from the other halogens, since the other halogen salts of palladium are soluble. It is difficult to precipitate the palladium quantitatively, because the iodide is very soluble in the presence of an excess of potassium iodide. Carbon monoxide unites with platinum chloride forming **carbonyl platinum chlorides**,  $\text{CO} \cdot \text{PtCl}_2$ ;  $2\text{CO} \cdot \text{PtCl}_2$ ;  $3\text{CO} \cdot \text{PtCl}_2$ ; carbon monoxide also reduces a solution of the chloride even in the cold.

**Chloroplatinites**

When platinum dichloride is digested with hydrochloric acid, it furnishes a reddish-brown solution which is supposed to contain **hydrochloroplatinous acid**,  $\text{H}_2\text{PtCl}_4$ . The acid has not been isolated, but the salts—chloroplatinites—are formed by treating the solution with, say, potassium chloride. **Potassium chloroplatinite**,  $\text{K}_2\text{PtCl}_6$ , forms rose-red crystals. The same salt is formed by reducing potassium chloroplatinate with moist cuprous chloride,  $\text{CuCl}$ . Potassium chloroplatinite is used in platinum printing in photography. This chloride is reduced to metallic platinum by the action of light on ferrous oxalate. Palladium forms a similar series of chloropalladites.

**Platinum-ammonia Compounds**

The platinum metals behave in a peculiar manner with ammonia. Thus, when ammonia is added to a solution of platinum tetrachloride,  $\text{PtCl}_4$ , in hydrochloric acid, a green precipitate is formed. If the mixture be boiled, a green insoluble compound,  $\text{Pt}(\text{NH}_3)_4 \cdot \text{PtCl}_4$ , called **Magnus's green salt**, is formed and  $\text{PtCl}_2 \cdot 2\text{NH}_3$  remains in solution. If the precipitate be heated to  $250^\circ$ , a yellow crystalline substance sparingly soluble in water is formed,  $\text{PtCl}_2 \cdot 2\text{NH}_3$ . Both compounds can be oxidized with chlorine to  $\text{PtCl}_4 \cdot 2\text{NH}_3$ . These two compounds may be taken to represent two well-defined series of platinum-ammonia compounds. One series is derived from  $\text{PtCl}_2$  and the other from  $\text{PtCl}_4$ . These will be discussed very shortly along with other complex amines, etc.

A solution of platinum salts gives a brown precipitate of the sulphide when treated with hydrogen sulphide, and the precipitate is soluble in alkali sulphide solution. Platinum salts also give a yellow crystalline precipitate with ammonium or potassium chloride. Most platinum salts decompose when ignited, and the metal is obtained on washing away the soluble products of decomposition. The metal itself is not affected by treatment with the mineral acids, although it is dissolved by aqua regia. Most platinum salts in solution are reduced by reducing agents.

## § 25 Complex Compounds of the Elements of Group VIII and Similar Substances

Many compounds are known, such as the ferrocyanides and ferricyanides, potassium cobaltinitrite and the amines of chromium, cobalt, platinum, etc., which presented great difficulties in formulation according to the usual valencies

of the elements concerned. Thus, the formula for potassium ferrocyanide will only fit in with the usual valencies of potassium (one), iron (two or three) and the cyanogen radical (one) if it be written  $4\text{KCN} \cdot \text{Fe}(\text{CN})_6$ , that is, as an ordinary double salt. But there are several facts about the behaviour of this substance which render this formula unsatisfactory; in particular, it does not give the reactions of cyanides, but appears to furnish a tetravalent anion  $[\text{Fe}(\text{CN})_6]^{4-}$ .

Similar problems occur in even more acute form when the complex metallic amines are considered, for additional peculiarities are noticeable. For example, in some of these, only a proportion of the acid radical present is detectable as such; thus with some complex chloride derivatives only a portion of the chlorine is precipitated by addition of silver nitrate solution. Compounds in which this behaviour is observable have already been noticed, e.g., the chromic chlorides (page 874). Again some complex derivatives are known whose solutions do not conduct electricity, and hence furnish no ions, although made from ordinary salts, etc.

Werner was the first to systematize the compounds of this type in a satisfactory way. In its original form, his theory distinguished two kinds of valency which he termed main, or principal, and auxiliary valencies. According to this, primary valencies represent those manifestations of chemical affinity which enable the combining capacities (valencies) of the elements to be expressed in terms of hydrogen atoms or their equivalents, e.g.,  $\text{Cl}-$ ,  $\text{Na}-$ ,  $\text{NO}_2-$ ,  $\text{CH}_3-$ , . . .

Auxiliary valencies similarly represent those manifestations of (residual) chemical affinity which are able to bring about the stable union of molecules as if the molecules were themselves radicals able to exist as independent molecules, e.g.,  $\text{H}_2\text{O}-$ ,  $\text{NH}_3-$ ,  $\text{HCl}-$ ,  $\text{CrCl}_3-$ , . . .

In illustration, antimony pentachloride,  $\text{SbCl}_5$ ; sulphur tetrachloride,  $\text{SCl}_4$ ; phosphorus oxychloride,  $\text{POCl}_3$ ; phosphorus pentachloride,  $\text{PCl}_5$ ; and hydrogen cyanide,  $\text{HCN}$ , may all be regarded as compounds in which the primary valencies of the elements are exhausted, yet, in virtue of their residual affinity, compounds like  $\text{SbCl}_5 \cdot 4\text{H}_2\text{O}$ ,  $\text{SbCl}_5 \cdot 3\text{HCN}$ ,  $\text{SbCl}_5 \cdot \text{SCl}_4$ ,  $\text{SbCl}_5 \cdot \text{PCl}_5$ ,  $\text{SbCl}_5 \cdot \text{POCl}_3$ , etc., are readily formed.

At a later stage, Werner came to the conclusion that the difference between principal and auxiliary valencies is not so marked as he had at first supposed, and is one of degree rather than of kind. This is supported by modern electronic views of valency (see below).

Werner considered that when the binding capacity of an elementary atom appears exhausted, it can still link up or co-ordinate with other molecules, and build up more complex structures, but that there is an upper limit to this process. The maximum number of atoms, radicals or molecular groups—independently of their valencies—which can be directly linked with a central atom he called the **co-ordination number** of that atom.

The co-ordination number of most atoms, curiously enough, is six; in a few cases it is four; and with molybdenum and the addition products of the chlorides of the alkaline earths, the co-ordination number appears to be eight. The fact that the co-ordination number for so many elements is six, and is generally independent of the nature of the co-ordinated groups, has made Werner suggest that the number is decided by available *space* rather than affinity and that six is usually the maximum number which can be fitted about the central atom to form a stable system. Consequently the co-ordination number represents a property of the atom which enables the constitution of "molecular compounds" to be referred back to actual linkings between definite atoms.

When the co-ordination number is six, Werner suggested, consequently, that the atoms or groups arrange themselves symmetrically about the central atom in the form of an octahedron. Evidence for the correctness of this assumption is given below. Similarly, when the co-ordination number is four, either a plane or a tetrahedral arrangement is theoretically possible. Examples of both arrangements are known.

The central atom with its surrounding co-ordinated atoms or groups constitutes, according to Werner, a unit which is not a salt (hence it does not itself ionize),

but it may be a radical which can combine with other radicals to form a salt-like compound. The effective valency of the co-ordinated group depends both in magnitude and sign upon the nature of the atoms or groups attached to the central atom, as can be seen from the examples quoted below.

In illustration of the way in which Werner's theory systematized the formulation, and hence advanced the comprehension, of these complex compounds, some platinum-ammines may be mentioned, and also some of the cobalt derivatives.

Thus, two well-defined series of platinum-ammines are known, derivable respectively from platinous and platonic chlorides, in which the co-ordination numbers are respectively four and six. Thus.

TABLE LXX.—PLATINUM-AMMINES DERIVED FROM PLATINOUS CHLORIDE

Empirical formula	Werner's formula	Effective valency of complex	Proportion of ionizable chlorine, etc.
$\text{Pt}(\text{NH}_3)_4\text{Cl}_2$	$[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$	+2	the whole
$\text{Pt}(\text{NH}_3)_3\text{Cl}_3$	$[\text{Pt}(\text{NH}_3)_3\text{Cl}]\text{Cl}_2$	+1	half
$\text{Pt}(\text{NH}_3)_2\text{Cl}_4$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	0	none. non-electrolyte
$\text{Pt}(\text{NH}_3)\text{Cl}_5\text{K}$	$[\text{Pt}(\text{NH}_3)\text{Cl}_3]\text{K}$	-1	none: one K' ion
$\text{PtCl}_6\text{K}_2$	$[\text{PtCl}_6]\text{K}_2$	-2	none: two K' ions

TABLE LXXI.—PLATINUM-AMMINES DERIVED FROM PLATINIC CHLORIDE

Empirical formula	Werner's formula	Effective valency of complex	Proportion of ionizable chlorine, etc.
$\text{Pt}(\text{NH}_3)_6\text{Cl}_4$	$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	+4	the whole
$\text{Pt}(\text{NH}_3)_5\text{Cl}_5$	$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$	+3	three-quarters
$\text{Pt}(\text{NH}_3)_4\text{Cl}_6$	$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$	+2	one-half
$\text{Pt}(\text{NH}_3)_3\text{Cl}_7$	$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$	+1	one-quarter
$\text{Pt}(\text{NH}_3)_2\text{Cl}_8$	$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	0	none: non-electrolyte
$\text{Pt}(\text{NH}_3)\text{Cl}_9\text{K}$	$[\text{Pt}(\text{NH}_3)\text{Cl}_5]\text{K}$	-1	none: one K' ion
$\text{PtCl}_{10}\text{K}_2$	$[\text{PtCl}_6]\text{K}_2$	-2	none: two K' ions

The simple or compound radicals which form the complex represented within the square brackets, are directly united with the central atom of platinum. The complex takes part in chemical reactions as if it were one individual radical. The basic ammonia in the complex can be successively replaced by acidic radicals—Cl, Br, NO<sub>2</sub>, CO<sub>3</sub>, SO<sub>4</sub>, etc.—until the complex becomes acidic instead of basic and the platonic ammine complexes finally pass from electronegative (basic) radicals to electropositive (acidic) radicals. Potassium chloroplatinate is the limit of the platonic ammines and potassium chloroplatinite is the limit of the platinous ammines. It will be obvious that an enormous number of derivatives is conceivable and, in fact, a very large number indeed is known, derived not only from platinum, but also from chromium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum.

#### Nomenclature of the Metal Ammines

Werner's system of naming the metal-ammonia compounds has been almost universally adopted. The constituents of the complex are taken first; and of these, the acid radicals with the suffix "o" come first; then follow any groups which behave like ammonia, e.g., H<sub>2</sub>O is called *aquo*; NO<sub>2</sub>, *nitrito* or *nitro*; NO<sub>3</sub>, *nitrate*; CO<sub>3</sub>, *carbonate*; SO<sub>3</sub>, *sulphite*; SO<sub>4</sub>, *sulphate*; SCN, *thiocyanate*; etc. And lastly, preceding the metal itself, the ammonia molecules are designated

"ammines," and spelt with a double "m" to distinguish the word from the "amines" or substituted ammonias. The prefixes di, tri, . . . indicate the number of each. The whole is written as one word.

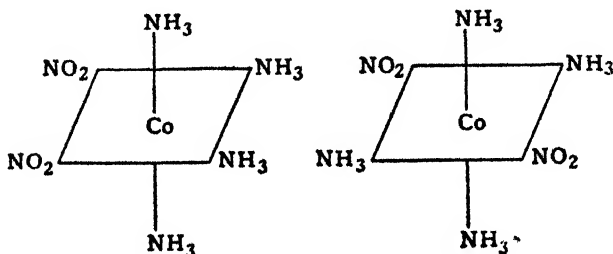
As examples of this nomenclature, the second and third compounds in each of the above tables may be taken. These will be, according to Werner's system:

Chlorotriamminoplatinous chloride,  
Dichlorodiammino platinum,  
Chloropentammino platinic chloride,  
Dichlorotetrammino platinic chloride.

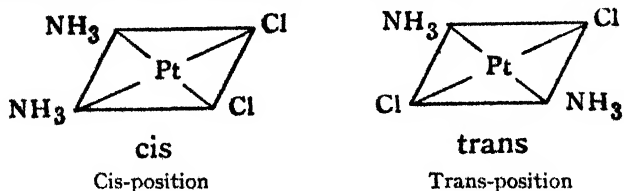
The valency of the complex is numerically equal to the difference between the ordinary valency of the central atom and the number of negative (acidic) groups or elements attached to the metal. Thus, the normal valency of platinum in the compounds of Table LXXI is 4, hence the valency of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}]$ , with one negative (acidic) group "Cl," will be 3; this means that the complex in question acts as a tervalent electropositive (basic) radical; and it can unite with three univalent electronegative (acidic) radicals. The valency of  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]$  with five negative (acidic) groups, "Cl," will be  $-1$ . This means that the complex under consideration will act as a univalent electronegative (acidic) radical, and it can accordingly unite with one electropositive (basic) radical like potassium, sodium, etc. If the valency of the acidic radicals in the complex are numerically equal to the normal valency of the central atom, the complex will be nullvalent. This is the case, for instance, with the complex  $[\text{Pt}(\text{NH}_3)_4\text{Cl}_4]$ .

One of the features of Werner's theory was that it provided an explanation of the isomerism which exists among some of these complex compounds, and also predicted the existence of isomers of types which had not previously been observed.

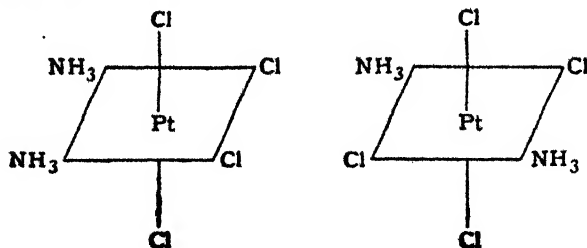
Thus, dinitritotetramminocobaltic chloride exists in two forms, the flaveo (golden-yellow) and croceo (saffron) forms. These are accounted for satisfactorily by Werner's assumption of an octahedral configuration for the complex; thus:



Again, there are two isomers of dichlorodiammineplatinum and two isomers of tetrachlorodiammineplatinum. In the former,  $[\text{Cl}_2\text{Pt}(\text{NH}_3)_2]$ , the four radicals are attached to the central atom of platinum in pairs. If the four groups were attached in space, say at the angular points of a regular tetrahedron, isomerism could hardly be expected because the four groups could be interchanged without altering their relations one with another. Hence it is inferred that the groups are arranged about the central atom of platinum in one plane. The resulting isomerism can be illustrated graphically by the schemes:



Similarly, on the assumption of an octahedral arrangement, the two isomers of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$  can be represented by:



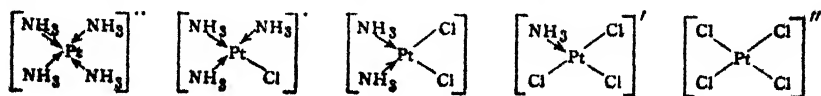
Werner has also applied this theory to salt hydrates, alums, etc., but its principal importance has lain in its elucidation of the structure of compounds of the types discussed above, and those represented by such substances as potassium mercuriiodide, cuprammonium sulphate, potassium cobalticyanide, etc.

## § 26 The Electronic Theory of Valency and Werner's Theory

The enunciation of Werner's theory was a great step forward, and gave a considerable stimulus to the investigation of complex compounds, but it was not until the modern theory of the structure of the atom (page 154) came to be applied to the problem of valency that any satisfactory explanation for the peculiar behaviour of what became known as the Werner compounds could be given.

Consider, for example, the platinum amines.

In the platinous amines, starting with the central platinous ion with a group of four valency electrons, the tetrammine is formed by the introduction of four ammonia molecules, in which each molecule shares a pair of electrons with the platinum atom by means of a duplet linkage. The total number of electrons associated with the platinum atom (atomic number 78) is thus  $78 - 2 + 8$ , i.e., 84, which is presumably a stable group. If one of the ammonia molecules be replaced by, say, a neutral chlorine atom, the ammonia molecule taking away with it two shared electrons, and the chlorine atom bringing in only one electron, means that there is an electron short. This is made good by the complex bringing in an electron from outside, thus reducing the positive charge of the complex by one unit. In that way,  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  passes into  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ , and so on with successive replacements of  $\text{NH}_3$ -groups by  $\text{Cl}$ -atoms, until, at the limit, a chloroplatinite,  $[\text{PtCl}_4]^{--}$ , say potassium chloroplatinite,  $\text{K}_2[\text{PtCl}_4]$ , is formed.



The symbol  $\rightarrow$  is used to indicate a valency bond in which two shared electrons are supplied by one atom, or atomic group, as donor, and the symbol  $—$  for an ordinary valency bond formed by two atoms sharing a pair of electrons. Similar results apply to the platonic amines where the central platinum ion, in forming the hexammine, for example, takes up six ammonia molecules and so forms the group of 86 electrons associated with the platinum atom; again presumably a particularly stable group. The maintenance of this number accounts for the behaviour summarized in Table LXX.

Similar considerations apply also to the ferrocyanides, ferricyanides, cobaltinitrites and, in fact, to the complex compounds in general.

The electronic theory of valency thus has the merit of being able to explain



the formation and behaviour of the complex (or Werner) compounds, along with the rest of chemical compounds, without resorting to any special assumptions. Its application to these substances also shows that Werner's original distinction between principal and auxiliary valencies can no longer be maintained, since, when established, a link is the same whether both of the electrons of the pair are derived from a single atom (co-ordinate link) or one from each of the two linking atoms (covalent link).

### § 27 Relationships of the Group VIII Elements

As mentioned in § 1 this group of Mendeléeff's Table differed from the others in consisting not of single elements, but of three triads of elements, and further, the members of each triad show much more closely related properties, and have atomic weights closer together than is usual in successive elements. The modern form of the Periodic Table indicates that these triads are the central ones of the transition elements of the long periods so that the gradation of properties now recognized in these (horizontal) series would be expected to include the Group VIII elements. This is, in fact, the case, for the series, chromium, manganese, iron, cobalt, nickel, copper and zinc, shows a steady gradation of properties; likewise molybdenum (technetium), ruthenium, rhodium, palladium, silver and cadmium; and also tungsten, rhenium, osmium, iridium, platinum, gold and mercury.

All the elements of the group are metals of high melting point, which exhibit marked catalytic activity. They are all characterized by very variable valency, and the property of forming complex compounds is developed to a high degree with all of them.

Some of the physical properties of these elements are given in Table LXIX, page 941. Corresponding properties of iron, cobalt and nickel are given in Table LXXII. Close resemblances within the triads are thus observable, and similar resemblances are to be found in the chemical properties.

TABLE LXXII — PHYSICAL PROPERTIES OF THE IRON FAMILY

	Iron	Cobalt	Nickel
Atomic weight . . . . .	55.85	58.94	58.71
Specific gravity . . . . .	7.86	8.7	8.9
Atomic volume . . . . .	7.16	6.94	6.68
Melting point . . . . .	1535°	1492°	1453°
Boiling point . . . . .	2800°	3000°	2800°

In addition to these similarities, among the triads themselves there is also a certain amount of resemblance between each element and its vertical analogues, particularly the last two members in each case. Thus iron, ruthenium and osmium have certain common properties, as also have cobalt, rhodium and iridium; and nickel, palladium and platinum.

Iron, ruthenium and osmium all form dichlorides and trichlorides,

and these also form complex chlorides or double chlorides such as  $\text{FeCl}_3 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$  (or  $\text{K}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$ ),  $\text{K}_2\text{RuCl}_6$ ,  $\text{K}_2\text{OsCl}_6$ , etc. All three elements form monoxides and sesquioxides, and at any rate derivatives of dioxides. Ruthenium and osmium form complex cyanides analogous to the ferrocyanides; but do not give rise to analogues of the ferricyanides.

Interesting comparisons are possible between cobalt, rhodium and iridium. The stable chloride of cobalt is a dichloride, while the stable chlorides of the other two elements are trichlorides; all three form double halides such as  $\text{LiCoCl}_4$ ,  $\text{K}_3\text{RhCl}_6$ ,  $\text{K}_3\text{IrCl}_6$ . Only cobalt forms a monoxide, but there are sesquioxides and dioxides of all three, the last-named being slightly acidic in nature, which suggests thus a relationship to iron, ruthenium and osmium, and to chromium and manganese also. All three elements form similar sulphates, alums and double cyanides, as well as complex ammine-derivatives like those of palladium and platinum.

Nickel, palladium and platinum are similar in their power of occluding hydrogen (notably palladium); they all yield a dichloride, and palladium and platinum at least form double chlorides; these two also give rise to trichlorides and double salts derived therefrom. All three form monoxides and dioxides; the latter displaying feeble acidic properties; they all form double cyanides like  $\text{K}_2\text{Pt}(\text{CN})_4$ .

As regards horizontal relationships, iron, cobalt and nickel are all fairly hard and high-melting, decidedly paramagnetic, and exhibit similar variability of valency. They give rise to isomorphous and closely similar complex compounds, such as the complex cyanides, etc. According to the electronic theory, this similarity is due to their all having two electrons in the outermost valency group, differing only in the composition of the preceding electron group (see Table XII).

While there are thus many resemblances observable among the members of the group, there are also considerable differences noticeable. Thus, relationship between iron and platinum is somewhat remote, and as regards close resemblance, is almost confined to the ease with which all the metals of the group give rise to complex compounds. This difficulty, however, is no greater than is found in many other groups, and there are adequate reasons for considering all these metals together in one group when the great diversity of properties observed in the elements of other groups, is considered such as the inclusion of the halogens and manganese in one group.

## QUESTIONS

### CHAPTER 2

1. Cite briefly *two* pieces of evidence which help to indicate the real existence in matter of discrete entities described as atoms and molecules.

Explain by reference to the theory of atomic structure what is meant by the terms (i) atomic number, (ii) isotope, (iii) neutron.

Discuss how far the properties of the following compounds may be inferred from the modes of linkage of their component atoms: (a) magnesium oxide; (b) carbon tetrachloride, (c) ammonium chloride, (d) copper sulphate pentahydrate. (N.U.J.M.B.)

2. Three kinds of fundamental particles are of great importance in chemical theory. Name them and give their relative masses and charges.

What is meant by (a) the atomic number ( $Z$ ) and (b) the atomic weight ( $M$ ) of an element? For sodium  $Z = 11$  and  $M = 23$ ; how must the nucleus of this atom be built up? How is the fractional atomic weight of chlorine ( $\text{Cl} = 35.5$ ) explained? How does the explanation conflict with Dalton's concept of the nature of *atoms* and which other of his postulates concerning elements are no longer acceptable? (N.U.J.M.B.)

### CHAPTER 3

1. State Graham's Law of diffusion of gases, and give a qualitative explanation of it in terms of the kinetic theory.

Describe an experiment to demonstrate gaseous diffusion.

A certain volume of acetic acid vapour was found to diffuse in 9.68 minutes, whilst the same volume of oxygen, with the same experimental conditions, took 5 minutes to diffuse. What deductions can be made as a result of this experiment? (N.U.J.M.B.)

2. If you were provided with samples of two gases, what experiments would you carry out to compare their rates of diffusion?

A volume of oxygen diffused through a porous plug in 10 sec. while the same volume of another gas diffused (under the same conditions) through the plug in 9.35 sec. Suggest possible formulae for the gas.

Discuss some of the uses to which gaseous diffusion has been put. ( $O = 16$ .) (Cambridge Locals.)

3. State Dalton's law of partial pressures.

Explain the importance of the law in correcting to N.T.P. the volumes of gases collected over water.

At  $540^\circ \text{C}$ . and 200 atmospheres pressure ammonia is 80 per cent dissociated. Calculate the partial pressure of each gas in the equilibrium mixture.

Discuss, from the point of view of Le Chatelier's theorem, the variations in the partial pressures produced by changes of the total pressure. (Cambridge Locals.)

4. Describe how the absolute density of any one gas has been determined with great accuracy, and give an account of important discoveries which were a sequel to determinations of this type. (Oxford Locals.)

5. Suggest explanations for *four* of the following observations: (a) a liquid cools when it is placed in a draught; (b) gas cools when it expands adiabatically; (c) a wet solid dries more rapidly in an evacuated desiccator than in an ordinary one, even though the same desiccant is used in both; (d) very small particles of solids appear to undergo quite erratic motion when they are suspended in liquids or gases; (e) a rubber balloon filled with hydrogen slowly collapses when left in the air. (Oxford Univ.)

6. What assumptions are made in the kinetic theory of gases? How does this theory explain the following facts: (a) that equal volumes of all gases at the same

temperature and pressure contain the same number of molecules; (b) that the vapour pressure of a liquid depends only on its temperature; (c) that gases diffuse at rates inversely proportional to the square roots of their densities? (Oxford Univ.)

7. On the basis of the Kinetic Theory deduce the relationships between the pressure of a gas and the velocity and the density of its molecules. Calculate the molecular weight of an unknown gas which under precisely similar conditions takes 1.117 times as long as oxygen to diffuse through an aperture. (Sheffield Univ.)

8. How do you understand that the principle of the Conservation of Energy applies to a case in which a coiled spring (as of brass) is compressed within a vessel of glass or porcelain, and then completely dissolved in acid? (Massachusetts Inst. of Technology.)

9. What do you understand by the kinetic theory of gases? How can you utilize your knowledge to formulate a proof of Avogadro's Hypothesis? (Punjab Univ.)

10. Under what conditions do gases exhibit deviations from Boyle's Law? To what factors do you attribute the deviations, and on what lines has the attempt been made to give a quantitative account of them? (London B.Sc.)

11. Explain why temperature is defined in terms of the properties of a perfect gas. (Oxford Univ.)

12. Describe how real gases are found to deviate from the ideal gas laws. Discuss how far these deviations are accounted for by the theory of Van der Waals. (Oxford Univ.)

13. Give an account of the work of (a) Andrews, (b) Faraday, (c) Dewar, on the liquefaction of gases. Describe some modern technical applications of liquid gases. (London B.Sc.)

14. Deduce a relationship between the pressure and velocity of the molecules of a perfect gas.

Calculate the root mean square velocity of an oxygen molecule at  $0^{\circ}\text{C}$ . at 760 mm. (Density of mercury = 13.6 gm./ml.) (Oxford Scholarships.)

15. Explain from first principles why the rate of effusion of carbon dioxide through a small orifice is slower than that of nitrogen. Sketch an apparatus for measuring this rate quantitatively. (Oxford Scholarships.)

16. What is a perfect gas? Why do real gases deviate from ideal behaviour and what is the importance of measurements of the deviations? (Oxford Scholarships.)

#### CHAPTER 4

1. Distinguish as clearly as you can between changes in matter which are classed as chemical and those classed as physical. Which of the following do you think are chemical, and which are physical: freezing ice-cream; souring milk; burning a candle; distilling water; magnetizing iron; electrolysis of a solution of copper sulphate?

2. Give a brief account of the Atomic Theory together with its history. (Princeton Univ.)

3. Trace the development and application in chemistry of the law of conservation of mass, dealing especially with the scope and degree of precision of the experimental evidence on which it is based. (London B.Sc.)

4. Define the laws of definite and multiple proportions. Show how the following analysis of three oxides of nitrogen illustrates the law of multiple proportions.

	A	B	C
Nitrogen	63.65	46.68	25.94
Oxygen	36.35	53.32	74.06

(Manchester Univ.)

5. What is meant by a chemical change? In what respects does chemical action differ from gravitation? What properties of matter do we define as chemical properties, and what are physical properties? (Punjab Univ.)

6. Explain clearly why you believe in the existence of atoms. (Oxford Scholarships.)
7. State the Law of Conservation of Mass and describe experiments which have been made in support of it. Indicate to what extent, if any, modern views of the nature of matter have modified belief in this law.
8. Describe in detail how you would separate the constituents of ordinary gunpowder, and ascertain the percentage of each constituent in the mixture. (St. Andrews Univ.)

#### CHAPTER 5

1. State Avogadro's hypothesis. Outline the experimental method and theoretical deductions which led to the conclusion that the hydrogen molecule contains two, and only two, atoms.

Explain how it is possible to use this conclusion to find the atomic weight of an element which forms volatile compounds.

196.5 c.c. of the vapour of a volatile metal, measured at 600° C. and 760 mm. pressure, weighed 0.55 grm. Calculate the molecular weight of the vapour of the metal. (N.U.J.M.B.)

2. Describe *one* method of measuring the vapour density of a substance, and indicate its advantages and limitations. Explain how the vapour density is related to the molecular weight of a substance. (Oxford Univ.)

3. Review briefly the various methods by which Avogadro's Number has been evaluated. (Inst. of Chem.)

4. 0.6 grm. of a liquid when vaporized at 150° C. and at a pressure of 750 mm. occupied 176 c.c. What is the value of (a) its vapour density referred to hydrogen, (b) its molecular weight? (London Inter B.Sc.)

5. Describe one method you would use to measure the vapour density of a given liquid. Explain why this value enables you to deduce the molecular weight of the substance in the form of vapour. (London Inter B.Sc.)

6. State Avogadro's hypothesis. Explain how experiments on the composition by volume of hydrogen chloride have led to the conclusion that the molecules of hydrogen and chlorine contain at least two atoms. (London Inter B.Sc.)

7. At 0° C. the vapour pressure of water = 4.62 mm., and that of a solution of 2.28 grm. of  $\text{CaCl}_2$  in 100 grm. of water = 4.584 mm. Calculate the degree of dissociation of the salt. (London B.Sc.)

8. Describe a method for the determination of molecular weights by the relative lowering in the vapour pressure of a pure solvent, produced by a non-volatile solute.

#### CHAPTER 6

1. Describe how the accurate equivalent weights of (a) carbon, and (b) chlorine, may be determined. What further experimental evidence is required to fix the atomic weights of these elements? (Cambridge Locals.)

2. If provided with pure sodium bicarbonate, describe exactly how you would prepare (a) pure sodium carbonate, (b) one litre of decinormal sodium carbonate solution.

25 c.c. of a solution A of barium chloride and 50 c.c. of N/10 sodium carbonate solution were mixed, boiled, filtered, and the precipitate washed with distilled water. The unchanged sodium carbonate in the filtrate was equivalent to 23.6 c.c. of N/10 acid. Calculate the weight of barium chloride (as  $\text{BaCl}_2$ ) in one litre of A. (Oxford Locals.)

3. Explain the term "equivalent weight" as applied to a metal. Calculate the numerical value in each of the following cases:

- (a) aluminium; given that it burns with an increase of 88.8 per cent of its weight;
- (b) magnesium; which when treated with acids yields 922 c.c. of hydrogen (measured at S.T.P.) per grm. (Durham Inter B.Sc.)

4. Show that the formula  $\text{H}_2\text{O}$  best represents the formula for water, quite independently of the atomic theory.

## CHAPTER 7

1. What is meant by the "equivalent" of an element, and what relation does it bear to the atomic weight? (London Univ.)

2. An element may exhibit several combining or equivalent weights, but only one atomic weight. Explain this phenomenon clearly and briefly.

3. An oxide of a metal contains 48.0 per cent of oxygen. What is the exact equivalent of the metal? If the specific heat of the metal was found to be 0.123, what is the probable atomic weight and valency of the metal, and what would be the probable nature of the oxide? (Manchester Univ.)

4. Give an account of the methods employed in the accurate determination of atomic weights. (Durham B.Sc.)

5. State the law of Dulong and Petit, and explain its application. Discuss its limitations to the determination of atomic weights.

6. State the law of isomorphism, and give examples of its utility in fixing the atomic weights of the elements.

7. Explain the relationship between *atomic weight*, *valency*, and *equivalent weight*. How would you obtain these for (a) hydrogen, (b) nitrogen, (c) carbon tetrachloride? (Oxford Scholarships.)

8. State and explain the principles which have been used to determine the atomic weight of (a) an inert gas, (b) a solid non-metallic element, e.g., carbon or sulphur, and (c) a heavy metal. (O. & C.J.B.)

9. Discuss the use of the methods of (a) Dulong and Petit, (b) Cannizzaro, in determining atomic weights.

The fluoride of a metal occurring in Group VI of the periodic classification has a vapour density of 149. The percentage of fluorine in the fluoride is 38.3. Calculate the atomic weight of the metal. ( $F = 19.0$ .) (Cambridge Locals.)

10. Discuss with full details two different methods which have been used in the determination of atomic weights. (Durham B.Sc.)

11. Stas determined the atomic weights of chlorine, potassium, and silver, starting with pure potassium chlorate and metallic silver. Outline the experiments he performed and indicate how the atomic weights were calculated. (Oxford Locals.)

12. Outline the methods available for the determination of atomic weights.

13. The equivalent of a volatile metal is 100.3 and its specific heat is 0.033; 0.25 gm. of the metal occupies 79.5 c.c. at 500° and 760 mm. Calculate the atomic weight of the metal and the molecular weight of the metal in the vapour phase. (Oxford Univ.)

## CHAPTER 8

1. The atomic weight of an element M is 56. An oxide of this element is found to consist of 53.8 per cent metal, and 46.2 per cent oxygen. Calculate the formula of the oxide. (London Univ.)

2. Oxygen is to be obtained from mercuric oxide, or manganese dioxide, or from potassium chlorate. What is the cheapest method of making oxygen per litre, so far as raw materials are concerned, if 100 gm. of mercuric oxide cost 3s.; 1 kilo of manganese dioxide 1s. 8d.; and 1 kilo of potassium chlorate 9s. 2d.?

3. Explain in words the precise meaning of the expression, " $Mg + H_2SO_4 = MgSO_4 + H_2$ ." (Punjab Univ.)

4. Explain the connection between the terms Equivalent, and Atomic weight. 0.100 gm. of a metal gave on treatment with dilute acid 34.2 c.c. of hydrogen measured at S.T.P. Calculate the equivalent of the metal. What further information is required in order to deduce the atomic weight? (Aberystwyth Univ.)

5. Ten gm. of water are (a) decomposed by sodium, (b) passed as steam over red-hot iron, (c) decomposed by an electric current. What volume of gas under standard conditions is produced in each case?

6. C. Rammelsberg (1841) analysed a crystalline salt obtained by treating antimony pentasulphide with concentrated potassium hydroxide, and found: K, 23.40; Sb, 37.80; S, 18.19; O, 7.30; water, 13.30; and he considered these

numbers agreed satisfactorily with the formula  $K_2SbS_4 \cdot K SbO_3 \cdot 5H_2O$ . Is this formula in accord with the observed data?

7. Calculate the percentage composition of potassium nitrate, sulphuric acid, common salt, phosphine, manganese dioxide.

8. According to C. R. A. Wright (1874), "neither the molecular theory nor the atomic theory, generally so called, is taken for granted in the formation of chemical equations." Discuss this quotation.

9. State the law of diffusion of gases, and state carefully the ratio of the rate of diffusion of oxygen (molecular weight 32) to that of air (density 14.4).

10. Calculate the weight of anhydrous zinc sulphate and the volume of hydrogen at 29° C. and 735 mm. pressure produced by the action of dilute sulphuric acid on 12 grm. of zinc. Hydrated zinc sulphate on heating to 100° C. loses 37.64 per cent of water, and on heating to a higher temperature 6.27 per cent more. Calculate the simplest molecular formula for hydrated zinc sulphate and find how many molecules of water are lost in the first heating. (Cape Univ.)

### CHAPTER 9

1. Elements in the first short period of the Periodic Table (lithium to fluorine) show marked differences from the other elements in their respective groups. Illustrate this by reference to differences between (a) water and hydrogen sulphide; (b) the oxides of nitrogen and those of phosphorus; (c) one example from the compounds of chlorine and fluorine.

2. Illustrate the term "diagonal relationship" with reference to similarities between the chemistry of lithium and magnesium, beryllium and aluminium, and boron and silicon. (Inst. of Chem.)

3. From a consideration of their properties, and those of their compounds, justify the positions of the following elements in the Periodic Table: (a) barium, (b) phosphorus, (c) iodine.

4. Discuss the chemistry of *one* of the following elements in relation to its position in the Periodic Table: (a) tin, (b) tungsten, (c) tellurium. (Inst. of Chem.)

5. Give a historical account of the methods which have been adopted for the classification of the chemical elements. Indicate the advantages and disadvantages of each method. (London B.Sc.)

6. State the general characteristics of the magnesium-zinc-cadmium family of metals, and indicate their relationships with the alkaline earths on the one hand and to aluminium on the other. (Science & Art Department.)

7. Why is manganese included with chlorine in the same group of the Periodic Table? With what elements besides the halogens is manganese related, and how is this relationship displayed? (London Univ.)

8. Compare the commonest hydrides of fluorine, chlorine, oxygen, sulphur.

9. What grounds had Mendeléeff for predicting the existence of the elements gallium, scandium, and germanium? (Science & Art Dept.)

10. What substances stand on the borderline between metals and non-metals? Illustrate the facts that such classification is always approximate, and that nearly all the laws of chemical combination or chemical relations, are approximately true. (New Zealand Univ.)

11. The later elements of the groups IB and IIB of the Periodic Table are less metallic than the earlier elements, while the reverse is the case in groups IVB to VIIB. Give examples to illustrate this statement and suggest an explanation. (Oxford Scholarships.)

12. The atomic numbers of the inert gases are 2, 10, 18, 36, 54 and 86. Make use of this information in deducing.

(a) the properties of the elements having atomic numbers 15 and 56;

(b) the salient characteristics of the newly discovered elements astatine (atomic number 85) and francium (atomic number 87);

(c) the probable position in the periodic classification of a metallic element which has a specific heat of 0.057 and an atomic number between 47 and 52,

which forms two chlorides containing respectively 23.7 and 48.1 per cent of chlorine. (N.U.J.M.B.)

## CHAPTER 10

1. What is (a) a proton, (b) an electron, (c) a neutron? Show how these particles contribute to the atomic structure of magnesium (atomic number 12, atomic weight 24), and chlorine (atomic number 17, atomic weight 35). Explain how the proportions of the particles change when the atoms of these elements are converted into ions.

How do you account for the existence of chlorine atoms of atomic weight 37? (Cambridge Locals.)

2. Write an essay on isotopes. (Oxford Locals.)

3. How were isotopes discovered? Describe methods which are available for their separation. Show how radioactivity measurements may be used to determine Avogadro's number. (Oxford Univ.)

4. What was the experimental evidence which led to the realization of the existence of isotopes?

What do you understand by (a) half-life (of a radioactive element); (b) radioactive equilibrium? (Oxford Univ.)

5. Give a careful account of the physical evidence for atomic disintegration of the radioactive elements. Outline the chemistry of three of these. (Durham B.Sc.)

6. What do you understand by *radioactive equilibrium*, *group displacement law*, *disintegration constant*, and *half-value period*? (Oxford Univ.)

7. Discuss from the historical standpoint, and with regard to present conceptions, the use of the term "element." (London B.Sc.)

8. Write concise but full notes on *two* of the following:

(a) the determination of the atomic number,

(b) the separation of isotopes,

(c) the mass spectrograph. (Durham B.Sc.)

9. Survey the experimental evidence for the electron as an atomic-constituent, and indicate how the electrons in a given atom can be counted. (Durham B.Sc.)

10. What is the experimental evidence for the electron as a constituent of the atom? (Durham B.Sc.)

11. Survey the experimental evidence for the existence and relative abundance of isotopes. (Durham B.Sc.)

12. Give an account of the recent determinations of the atomic weight of lead, and explain the probable reason for the different values obtained with lead obtained from different sources. (London B.Sc.)

13. Evaluate the importance of the discovery of the electron to the progress of chemistry. (Oxford Scholarships.)

## CHAPTER 11

1. Write an essay on "Covalent Bonds in Inorganic Compounds." (Oxford Univ.)

2. Discuss what you understand by the term "valency" by reference to the substances represented by the formulae:  $\text{KCl}$ ,  $\text{KO}_2$ ,  $\text{KN}_3$ ,  $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ ,  $\text{K}_2\text{Ni}(\text{CN})_4$ ,  $\text{Ni}(\text{CO})_4$ . (Inst. of Chem.)

3. Write an essay on "Electrovalency and Covalency." (Oxford Univ.)

## CHAPTER 12

1. Write briefly on *two* of the following:

(a) Mass defects in atomic nuclei: packing fractions.

(b) The natural disintegration of atomic nuclei.

(c) Nuclear fission. (Inst. of Chem.)



CHAPTER 13

1. Explain what is meant by a solubility curve. How would you obtain such a curve for potassium nitrate and water? Show how solubility curves may be used to investigate the possibility of separating two soluble salts by fractional crystallation. (Oxford Scholarships.)

2. Define "Saturated Solution," "Supersaturated Solution," and "Solubility," as applied to a solid dissolved in a liquid.

How may the solubility of oxalic acid in water be determined at 35° C.?  
50.42 grm. of a saturated solution of a certain sulphate (Formula Weight = 159.8) saturated at 20° C. were made up 250 c.c. 25 c.c. of this diluted solution give 1.265 grm. of barium sulphate when treated with barium chloride solution. Determine the solubility of the original sulphate at 20° C.

At 40° C. the solubility is 28.5 grm. per 100 grm. water. Deduce whether the process of solution in this case is exothermic. (N.U.J.M.B.)

3. State the assumptions on which the Kinetic Theory of gases is based.

How is this theory extended to explain qualitatively (a) the vapour pressure of a pure liquid and its variation with temperature, (b) the vapour pressure of a solution containing a non-volatile solute and its variation with concentration?

A solution of 6.75 grm. of a non-volatile substance X in 37.0 grm. of ether has a vapour pressure of 500 mm. mercury at the temperature at which ether has a vapour pressure of 550 mm. Calculate the molecular weight of X. (N.U.J.M.B.)

4. Discuss briefly the methods available for determining the solubility of (a) gases in liquids, (b) solids in liquids.

A saturated aqueous solution of a non-electrolyte, of molecular weight 180, exerted an osmotic pressure of 0.516 atmospheres at 22° C. What is the solubility of the substance in grams per litre of water at this temperature? (Cambridge Locals.)

5. Review the factors affecting the equilibrium set up in the following systems:

(a) the dissociation of calcium carbonate;

(b) rhombic sulphur—monoclinic sulphur,

(c)  $\text{HCO}_3^- + \text{H}^+$  in aqueous solution;

(d) sodium carbonate decahydrate—anhydrous sodium carbonate

X is a weak tribasic acid (mol. wt. = 210) which is soluble in benzene and water. After 2.800 grm. of X had been shaken with 100 c.c. benzene and 50 c.c. of water until completely dissolved, it was found that 25 c.c. of the aqueous layer required 14.50 c.c. of normal sodium hydroxide solution for neutralization. Calculate the ratio of the concentrations of X which are contained in equal volumes of benzene and water. (N.U.J.M.B.)

6. Define the terms: degree of freedom, phase, component, and variant, in Gibbs's rule. In the case of a system containing salt and water, and the phases, salt, saturated solution, and vapour, how many variants must be fixed in order to establish equilibrium? Discuss the reasons for your statement. (Sydney Univ.)

7. Describe how you would determine the solubility of a gas in water.

Assuming that, at 15° C. and 1 atmosphere pressure, (a) air is a mixture of 80 per cent  $\text{N}_2$  and 20 per cent  $\text{O}_2$ , (b) oxygen is twice as soluble in water as is nitrogen, calculate the percentage, by volume, of oxygen in the gases boiled out from water which has stood for some time in contact with the atmosphere at 15° C. (Cambridge Locals)

8. 100 grm. of water dissolve the following quantities of zinc sulphate at the temperatures named:

Temp. °C.	0	25	39	50	70	80	90	100
$\text{ZnSO}_4$	41.9	57.9	70.1	76.8	88.7	86.6	83.7	80.8 grm.

Plot the results on squared paper so as to show a solubility curve.

9. "Sodium sulphite  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , forms colourless *monoclinic crystals*, with a *saline taste and alkaline reaction*. The crystals *effloresce* in dry air: they are *soluble* in water: and become *anhydrous* when heated to 150° C. At a higher temperature the crystals *decompose*, forming a yellow liquid." Explain the words in italics in this quotation.

10. If the solubility of sodium chloride in water at 20° C. is 35.6, how much water will be needed at this temperature for the solution of a kilogram of the salt?

11. Water at 15° can absorb 756 times its volume of ammonia. What mass of ammonia can be dissolved in one litre at 15° under a pressure of 10 atmospheres, the volume of one gram. of ammonia at 0° C. and a pressure of 760 mm. being 1317 c.c.? (Sydney Univ.)

12. Explain the meaning of the terms, saturated solution, solution, and crystallization. Show how it can be proved experimentally that hot water is generally a better solvent than cold water. (Cape Univ.)

13. The absorption coefficient of nitrogen dissolved in water is 0.0152 at 12.6° C. What volume of the gas measured at standard temperature and pressure is absorbed by one litre of water at 12.6° C. at each of the following pressures: 1000 mm., 748.2 mm., 391 mm., and 14.3 mm.? (New Zealand Univ.)

14. Plot curves to represent the following tabulated numbers representing the number of gram. of salt in 100 gram. of water at the temperatures named:

Temp. °C.	0	10	20	30	40	50	60	70	80	90	100
Na <sub>2</sub> SO <sub>4</sub>	5.0	9.0	19.4	40.0	48.8	46.7	45.3	44.4	43.7	43.1	42.5
K-alum	3.9	7.5	15.1	22.0	30.3	44.1	66.6	90.7	134.5	209.3	257.5

Answer by reference to the resulting diagram; (a) two saturated solutions contain 26.5 gram. sodium sulphate and potash alum respectively in 100 gram of water. At what temps. were the two solutions made up? (b) a saturated solution of potash alum in 100 gram. of water was made up at 64° C. and another of sodium sulphate at 72° C. If both solutions were cooled to 15° C. how many more gram. of potash alum would separate out than of sodium sulphate? (Staffs. County Major Scholarship.)

#### CHAPTER 14

1. Describe an experiment to demonstrate the phenomenon of osmosis. A solution of 1 gram. of a substance X in 100 c.c. of water has an osmotic pressure of 595 mm. of mercury at 7°. What is the molecular weight of X? (Oxford Univ.)

2. Describe concisely *two* methods for determining the molecular weights of substances in solution.

A solution containing 11 gram. of barium nitrate in 100 gram. of water boils at 100.46° C. Calculate (a) the apparent molecular weight, and (b) the apparent degree of dissociation of the salt, in this solution.

(The molecular elevation constant for water is 0.52° C. for 1000 gram. of solvent.  $N = 14$ ;  $O = 16$ ;  $Ba = 137.4$ .) (O. & C.J.B.)

3. Define Osmosis, osmotic pressure of a solution.

*Either*, Show how you can demonstrate the existence of the former, and how the latter can be measured for an aqueous solution.

*Or*, Show how the osmotic pressure of a solution is related to the lowering of the vapour pressure of the solvent. (O. & C.J.B.)

4. What is meant by the vapour pressure of a liquid? Show how the vapour pressure of a solvent is altered by the pressure of a solute, and how vapour pressure measurements may be used to determine molecular weights. (Oxford Univ.)

5. Summarize briefly the methods by which the molecular weight of a substance in solution may be determined. Mention their limitations and choose *one* of the methods for more detailed discussion. (Inst. of Chem.)

6. When 0.3 gram. of a substance with molecular weight 150 is dissolved in 42 gram. of a certain solvent, the freezing point of the latter is lowered by 0.233° C. When 0.27 gram. of another substance is dissolved in 56 gram. of the same solvent the observed depression of the freezing point is 0.218° C. Calculate the molecular weight of the second solute. (London B.Sc.)

7. What is osmotic pressure? Has this any connection with the pressure of a gas? Alcohol is said to be normal in regard to its vapour pressure and its osmotic

pressure; ammonium chloride has an abnormal vapour pressure and osmotic pressure. Explain the meaning of the terms "normal" and "abnormal" used here. (Sydney Univ.)

8. Describe the effects produced by soluble and insoluble substances on the boiling and melting points of water. What explanation can be given of the differences observed when common salt and sugar are respectively dissolved in sufficient pure water to form dilute solutions of the same molecular concentration? To what other properties of solutions does this explanation apply? (Punjab Univ.)

9. Give an account of the procedure involved in the determination of the osmotic pressure of a concentrated solution of cane sugar. (London B.Sc.)

10. Give a precise account of the freezing of pure substances and of solutions of pure substances; showing in detail how the facts afford a quantitative knowledge of the condition of dissolved substances. (Durham Inter B.Sc.)

11. The aqueous solution of a certain non-electrolyte containing 0.3 gm. of the substance per 100 c.c. has an osmotic pressure of 81 mm. of mercury at 30° C. What is the molecular weight of the substance? (London B.Sc.)

12. Describe, with a diagram of essential apparatus, how you would determine the molecular weight of a substance in solution by the elevation of the boiling-point method, using the vapour of the solvent for heating purposes.

$w$  gm. of solute in  $V$  c.c. of solvent gave an elevation of  $\theta^\circ$  C. The elevation constant for 100 c.c. solvent being  $E^\circ$  C., deduce from first principles the molecular weight of the solute.

Explain how it is possible for the vapour of a liquid boiling at 100° C. to raise the boiling point of a solution to 101° C. (Oxford Locals)

#### CHAPTER 15

1. Give an account of the ionic theory of solution, stating clearly the facts on which it is based. (Aberystwyth Univ.)

2. H. J. Gladstone and W. Hibbert (1889) passed the same current of electricity through solutions of zinc and silver salts, and obtained quantities of these metals in the ratio  $\text{Zn} : \text{Ag} = 1 : 3.298$ . If the equivalent of silver is 107.88, what is that of zinc?

3. Outline the evidence upon which our present ideas about the nature of solutions of salts in water are based. (Oxford Scholarships.)

4. Describe and explain what happens when a solution of copper sulphate is electrolysed using (a) copper, (b) platinum electrodes

State which electrode is the anode and which is the cathode. (Oxford Univ.)

5. By what experiments would you demonstrate the theory of dissociation of salts? If a gram-mol weight of (a) copper sulphate, (b) acetic acid, (c) hydrochloric acid were dissolved severally in a litre of water, in what ways would the physical properties of the three solutions differ? (Oxford Univ.)

6. What is the Electrochemical Series and how does it help to explain the differences in the behaviour of various elements towards water, acids, and alkalis? (Oxford Univ.)

7. State Faraday's Laws of Electrolysis. What correspondence, if any, can you find between them and the laws of chemical combination, and how far do they indicate the electrical character of atomic structure?

From what sources can evidence be obtained of the existence of ions in solution? (O. & C.J.B.)

8. Calculate the approximate pH values of the solutions obtained by adding 20, 24, 24.9, and 25 c.c. of decinormal sodium hydroxide to 25 c.c. of decinormal hydrochloric acid. Why would the values be different if decinormal acetic acid were used instead of hydrochloric, and what would be the effect in each case if ammonium hydroxide were substituted for sodium hydroxide? (O. & C.J.B.)

9. Describe how you would measure the specific conductivity of a given solution at 25° C.

Discuss the importance to the chemist of conductivity measurements. (Oxford Locals.)

10. Discuss the meaning of the term "electrochemical series." Arrange the elements calcium, copper, iron, magnesium, potassium and zinc in an order which illustrates the series.

Justify the order you give by considering the behaviour of each of these elements towards water (or steam). (N.U.J.M.B.)

11. Describe simple experiments you would make to place the metals zinc, magnesium, calcium, and copper in their correct order in the electrochemical series.

Often the more electropositive elements have the more basic oxides. Discuss this statement in connection with the above four metals. (Cambridge Locals.)

12. Explain what is meant by the equivalent conductivity of a solution, and describe briefly how this quantity varies with concentration for different types of electrolyte.

How may measurements of conductivities be used to determine the solubility of barium sulphate? (Cambridge Locals.)

13. What do you understand by (a) specific conductivity, (b) equivalent conductivity? The specific conductivity of a saturated solution of silver chloride was found to be  $1.25 \times 10^{-6}$  mhos. Calculate the solubility of silver chloride, taking the equivalent conductivity at infinite dilution of hydrochloric acid to be 380.4, of silver nitrate to be 115.4 and of nitric acid to be 376.8 mhos. (Oxford Scholarships.)

14. State Faraday's Laws of Electrolysis.

Give equations for the reactions which take place when a solution of sodium chloride is electrolysed with inert electrodes under various conditions.

The impure copper anode of a copper voltameter lost 3.76 gm. in weight on electrolysis. The same current passed for the same time through acidified water resulted in the collection of 594 ml. of oxygen at  $14^{\circ}\text{C}$  and 751 mm. Calculate the percentage purity of the copper anode, assuming that only copper passes into solution. (Saturated vapour pressure of water at  $14^{\circ}\text{C}$  = 12 mm. Hg.) (Cambridge Locals.)

15. What is meant by electrolysis? Illustrate your answer by reference to the electrolysis of aqueous solutions of metallic salts. (St. Andrews Univ.)

16. A current passes simultaneously through acidulated water, a solution of copper sulphate, and molten silver chloride. What substances are produced in each cell, and how many gm. of each in the time that 10 c.c. of hydrogen are liberated from water? (New Zealand Univ.)

17. One and the same electric current is simultaneously passed through solutions of (a) hydrochloric acid, (b) copper sulphate, (c) silver sulphate. Draw a diagram of the apparatus required, and indicate what products would be obtained in each case. Calculate also the weights of these products which would be formed during the time that 1000 c.c. of dry hydrogen (at N.T.P.) were collected from the hydrochloric acid solution. (London Univ.)

18. Describe with practical details the determination of the electrical conductivity of an aqueous salt solution.

A potential difference of 20 volts applied to the end of a column of N/10 silver nitrate, 4 cm. in diameter, and 12 cm. in length, gives a current of 0.198 amp. Calculate the specific and equivalent conductivity of the solution. (London B.Sc.)

19. Outline the evidence for the existence of ions in aqueous solutions of electrolytes. (Durham Inter. B.Sc.)

20. How do you account for the difference in the nature of the products of electrolysis of a given substance with electrodes of different materials? Illustrate your answer by reference to the electrolysis of sodium chloride and copper sulphate.

21. Explain the nature of the observations which lead to the belief that salts in solution are largely split up into ions. (Oxford Scholarships.)

22. What is meant by the electrochemical series of the elements? How is it obtained and of what use is it? (Oxford Scholarships.)

CHAPTER 16

1. Describe briefly, with suitable examples, how the heats of formation of compounds can be determined. What is the value of a knowledge of these quantities?

What interest attaches to the heats of neutralization of acids by bases? (Oxford Univ.)

2. Define (a) exothermic reaction, (b) heat of solution, (c) heat of formation. Name and define the unit in which heat is usually expressed in chemical problems.

(i) State Hess's Law of Constant Heat Summation.

(ii) Explain why the heat of neutralization of any strong acid by any strong base is the same.

(iii) Explain why heat is evolved when many electrolytes dissolve in water although it would be expected that the work done in separating their ions would be revealed by the absorption of heat.

The heats of formation of steam and ferrosioferric oxide,  $\text{Fe}_3\text{O}_4$ , are respectively 57.8 and 166.9 units evolved. Calculate the heat of the reaction between this oxide and hydrogen to give iron and steam. (N.U.J.M.B.)

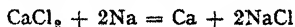
3. State Hess's Law. Define the terms (a) heat of formation, (b) heat of neutralization.

(i) Why is the heat of reaction between ammonia and hydrogen chloride gases different from the heat of reaction when they are in solution?

(ii) Why are the heats of neutralization, in aqueous solution, of nitric acid with sodium hydroxide and nitric acid with potassium hydroxide, respectively, almost identical?

(iii) Why is the heat of neutralization, in aqueous solution of nitric acid with ammonia different from those in (ii)?

(iv) Given the values of the heats evolved in the formation of calcium chloride (170,000 cal. per gm.-mol.) and of sodium chloride (97,800 cal. per gm.-mol.) calculate the heat change in the reaction of



stating precisely whether this heat is evolved or absorbed. (N.U.J.M.B.)

4. The heats of formation of ferric oxide and aluminium oxide being 195,600 cal. and 923,600 cal. respectively, calculate the heat of reduction of ferric oxide by aluminium. (London B.Sc.)

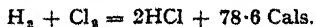
5. How may a chemical reaction be modified so as to represent not only a redistribution of matter, but also a redistribution of energy? Explain what is meant by the heat of formation of a compound. From the following data, find the heat of formation of acetylene. When 24 grm. of carbon, 2 grm. of hydrogen, and 26 grm. of acetylene are burnt separately in an excess of oxygen, 194,000, 68,000, and 310,000 cal. are respectively evolved. (Cape Univ.)

6. What amount of heat is evolved when 46 grm. of metallic sodium react with an excess of water, given the heats of formation of water as 69 Cals., and of sodium hydroxide 112.5 Cals.?

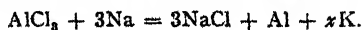
7. What is the heat of formation of zinc chloride in solution when the reaction is given by:



and the heat of formation of an aqueous solution of hydrogen chloride is given by the equation:



8. Find the amount of heat K liberated in the reaction,



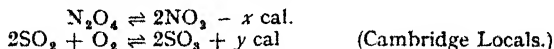
The heat of formation of aluminium chloride is 1610 K, and of sodium chloride, 976 K.

9. Find the heat of formation of acetaldehyde ( $C_2H_4O$ ) from its elements when it is (a) liquid and (b) gaseous.

Data:  $C_2H_4O + 5O = 2CO_2 + 2H_2O$ ;  
 $(C_2H_4O, 5O)$  liquid 275.5 Cals.;  $(CO_2)$  96.6 Cals  
 $(C_2H_4O, 5O)$  gaseous, 266.0 Cals.

### CHAPTER 17

1. Discuss the effects (if any) of (a) change of temperature, (b) change of pressure, (c) presence of a catalyst, on (i) the velocity of chemical reactions, (ii) the position of equilibrium in reversible reactions. Illustrate your answer by reference to the reactions represented by the following equations:



2. What do you understand by (a) the Law of Mass Action, (b) an equilibrium constant?

If the dissociation constant for acetic acid at  $18^\circ C$ . is  $1.8 \times 10^{-5}$  (concentrations being measured in gram equivalents per litre), calculate the concentration of hydrogen ions in a decinormal solution of acetic acid at  $18^\circ C$ . (O. & C. J. B.)

3. Define and give examples of thermal dissociation, kinetic equilibrium, reversible reaction, electrolysis, and reduction. (Princeton Univ.)

4. What do you understand by a reversible chemical reaction? Cite examples and point out the conditions affecting the course of the action. (St. Andrews Univ.)

5. The rate of chemical change may be altered by (a) temperature, (b) catalysis, and (c) solution. Describe accurately the experiment illustrating the change in rate of reaction which may be brought about by each of these factors. (London Univ.)

6. Manganese dioxide is said to catalyse the decomposition of potassium chlorate by heat. What do you understand by this? How would you find out whether cupric oxide was a catalyst in this reaction, and how would you compare its efficiency in this respect with that of manganese dioxide? (Oxford Scholarships.)

7. Outline the chief phenomena of catalysis, with reference to typical examples, and indicate the explanations of catalytic action which have been advanced. (Durham B.Sc.)

8. Write a historical essay on the Law of Mass Action. (London B.Sc.)

9. State the characteristic features of catalysis.

Define the following terms, quoting *one* example of each. (a) homogeneous catalysis, (b) heterogeneous catalysis, (c) catalyst poison, (d) autocatalysis.

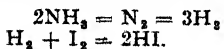
What influence has a catalyst on the composition of the final equilibrium mixture of a reaction?

Mentioning essential details, describe concisely how you would find out whether a given mineral acid acted as a catalyst for the hydrolysis of ethyl acetate by water. (N.U. J. M.B.)

10. Describe how the equilibrium between hydrogen, iodine, and hydrogen iodide could be measured at, say,  $300^\circ C$ . How would you expect this equilibrium to vary with (a) increasing temperature, (b) increasing pressure? Give your reasons. The reaction at  $300^\circ C$ . is slightly exothermic.

11. Outline the more important views upon the phenomena of catalysis, illustrating your answer by examples of industrial importance. (Inst. of Chem.)

12. State Le Chatelier's principle and explain the effect, if any, of decreasing (a) the pressure, (b) the temperature, on the following gaseous equilibria:



Explain (i) why a catalyst is used in the synthesis of ammonia, (ii) why the melting point of ice is lowered by an increase in pressure. (Oxford Locals.)

13. State the Law of Mass Action and show how you would use it to derive the equilibrium constant of a reaction



in which the reactants and resultants are all gases.

What steps could be taken (a) to obtain as large a yield as possible of  $C$  from a given amount of  $B$ , and (b) to obtain the yield as quickly as possible. (O. & C.J.B.)

14. Define and explain "solubility product." For what type of substance is this term used? What units are used in the quantitative expression of its solubility products?

If the solubility product of magnesium carbonate is  $2.5 \times 10^{-5}$ , calculate its solubility in water in gm.-mol. per litre.

The following are values of solubility products at  $18^\circ \text{C}$ : ferrous hydroxide,  $1.6 \times 10^{-14}$ ; ferric hydroxide,  $1.1 \times 10^{-38}$ ; magnesium hydroxide,  $1.2 \times 10^{-11}$ . The dissociation constant of ammonium hydroxide is  $1.8 \times 10^{-6}$ . Give the meaning of these statements and explain carefully their bearing on the procedure adopted in Group III in qualitative analysis. (N.U.J.M.B.)

15. Write down the expression for the equilibrium constant of the reaction



(a) If  $a$  is the fraction of ammonia present by volume in an equilibrium mixture made from one volume of nitrogen and three volumes of hydrogen, and  $P$  is the total pressure, show that  $a/(1-a)^2 = kP$ , where  $k$  is a constant. (It will be found convenient to express concentrations as partial pressures.)

If 0.25 of the equilibrium mixture at  $400^\circ \text{C}$ . and 100 atmospheres pressure is ammonia, calculate what fraction of the mixture will be ammonia at 10 atmospheres, at that temperature.

(b) The equilibrium constant varies with temperature according to the equation:

$$\log K_1 - \log K_2 = \frac{13,200}{2.303} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

where  $K_1$  and  $K_2$  are the constants at  $T_1$  and  $T_2$  respectively.

In the light of this equation and your results in (a) explain very briefly the conditions used in the manufacture of ammonia. Why is it necessary to use a catalyst? (O. & C.J.B.)

16. Discuss how temperature and pressure may affect (a) chemical equilibria, and (b) the rate of chemical reactions. Give examples to illustrate your answer. (Oxford Scholarships.)

17. Explain the considerations which decide the choice of the optimum temperature and pressure for a gas reaction. Illustrate your remarks by reference to the reactions used for making (a) ammonia, (b) nitric acid, (c) sulphur trioxide. (Oxford Scholarships.)

## CHAPTER 18

Draw and explain the curves showing approximately the change of pH when 50 c.c. of decinormal sodium hydroxide solution is run slowly with stirring into (a) 25 c.c. of decinormal hydrochloric acid, (b) 25 c.c. of decinormal acetic acid.

What light do the curves throw on the indicators which may be used for the titration of sodium hydroxide with these acids? Why is it not possible to titrate acetic acid with ammonium hydroxide, using ordinary indicators? (O. & C.J.B.)

2. How is the following phenomenon explained? When dilute solutions of any strong acid and base are mixed together in equivalent proportions, approximately the same amount of heat is given out (13,700 Cals.), although the heats of formation of the various salts formed have very different values. (Madras Univ.)

3. What is Ostwald's Dilution Law? Explain how it is applied to determine the dissociation constant of a weak acid, and describe the apparatus used for such a determination. (Oxford Scholarships.)

4. What is meant by the strength of an acid? Describe the different methods which have been employed in ascertaining the relative strength of two acids. (London B.Sc.)

5. What is an indicator? Give some account of the theory of indicators as employed in acidimetry and alkalimetry.

6. What is Ostwald's Dilution Formula for weak electrolytes? Deduce it theoretically, and explain clearly how the constant is experimentally obtained. (St. Andrews Univ.)

7. What do you understand by the term solubility product? The solubility of silver chloride in water at 20°C. is 1.507 mg. per litre. What would be the solubility in 0.001 M-potassium chloride? Assume both salts to be completely dissociated.

Explain why silver chloride dissolves in ammonium hydroxide but not in dilute hydrochloric acid, and why barium phosphate dissolves in hydrochloric acid but not in ammonium hydroxide. (Oxford Univ.)

8. State Faraday's Laws of Electrolysis.

Calculate the  $pH$  at 25°C. of a mixture of 59 ml. of N/5 acetic acid and 141 ml of N/5 sodium acetate, if the dissociation constant of acetic acid at 25°C. is  $1.8 \times 10^{-5}$ . (Oxford Univ.)

9. Illustrate what is meant by an "indicator" in volumetric analysis. Explain why most indicators can be used when titrating a strong acid with a strong base, though no indicator will give a sharp end point when oxalic acid is titrated with ammonia. (Oxford Univ.)

10. What is the "specific conductivity" and the "equivalent conductivity" of an electrolyte?

The equivalent conductivity of a N/32 solution of a weak acid is 9.2 reciprocal ohms. The equivalent conductivity at infinite dilution being 389 reciprocal ohms, find the dissociation constant of the acid. (Oxford Univ.)

11. In terms of the ionic theory, explain the fact that Ohm's law is obeyed accurately by solutions of electrolytes. Mention *three* other facts which support the theory.

What is the difference between a weak acid and a strong acid?

Given crystalline specimens of two acids, indicate how you would determine which is the stronger. (Cambridge Locals)

12. Define the term  $pH$ .

To 50 ml. of N. sodium hydroxide are added 100 ml. of N. acetic acid. Calculate the  $pH$ , given that the dissociation constant of acetic acid is  $1.8 \times 10^{-5}$ . Discuss qualitatively the effects of adding small portions of acid, or of alkali, to this final mixture. (Cambridge Locals.)

13. Calculate the  $pH$  at 25° of a decinormal solution of acetic acid, for which  $K_a$ , at this temperature, is  $1.8 \times 10^{-5}$ .

Describe how the  $pH$  varies during the titration of such a solution with a decinormal solution of sodium hydroxide, and discuss the choice of an indicator for this titration. (Cambridge Locals.)

14. 20 ml. of a 0.2N acid were titrated with sodium hydroxide solution and during the course of the titration the following measurements were made:

ml. NaOH added	$pH$	ml. NaOH added	$pH$
0	2.4	24	4.7
4	3.1	28	5.1
8	3.6	30	5.7
12	3.9	31	6.3
16	4.1	31.5	7.5
20	4.4	31.7	9.0

Plot, on squared paper, a titration curve, and deduce the dissociation constant of the acid. What is the normality of the alkali, and what indicator would be suitable for such a titration? (Cambridge Locals.)



15. Explain carefully from the standpoint of the ionic theory why dilute hydrochloric acid is added to a solution containing copper and nickel ions before passing hydrogen sulphide to precipitate copper as the sulphide.

Describe and explain what results you would expect (i) if dilute hydrochloric acid were not added before passing hydrogen sulphide, (ii) if acetic acid were used instead of dilute hydrochloric acid, (iii) if concentrated hydrochloric acid were used in place of dilute hydrochloric acid. (N.U.J.M.B.)

16. Define solubility product.

The solubility of silver chloride in water is 0.0015 gm./litre. Calculate its solubility product. What is the maximum concentration of silver ion that should be able to exist in a decinormal solution of hydrochloric acid? Why are "insoluble chlorides" often soluble in concentrated hydrochloric acid? How would you attempt to show the truth of your explanation? (O. & C.J.B.)

17. In terms of the ionic theory, what is a strong acid?—a strong base?—a weak acid?—a weak base? In these terms classify the following: HCl,  $\text{NH}_4\text{OH}$ , KOH,  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{Al}(\text{OH})_3$ . (Amherst Coll., U.S.A.)

18. Discuss, with examples, the difference between double salts and complex salts, and describe the preparation of one typical member of each class.

The freezing point of a molar solution of potassium iodide is  $-3.2^\circ$ . When mercuric iodide (which is insoluble in pure water) is added in excess, the freezing point of the solution is raised to  $-2.4^\circ$ . Comment on this result. (Cambridge Locals.)

19. Three solutions of hydrochloric acid which were 0.5N, 5.0N and 10N respectively were saturated with sodium chloride. 10 c.c. of each solution was then made up separately to 1 litre with distilled water, making solutions A, B, and C. 20 c.c. of each of these diluted solutions were titrated, after neutralization, with decinormal silver nitrate. Solution A required 11.5 c.c. of silver nitrate solution, solution B required 13 c.c., and solution C required 20 c.c. Calculate to the nearest gram how much sodium chloride had dissolved in one litre of each of the original hydrochloric acid solutions. Explain why the solubility of sodium chloride in hydrochloric acid varies, as your results indicate. (O. & C.J.B.)

20. Define and explain the term "solubility product." What is meant by the statement that the solubility product of silver chloride is  $1.2 \times 10^{-10}$  and that of lead iodide is  $1.4 \times 10^{-8}$ .

Make clear the differences between "solubility product" and "dissociation constant"

Explain why hydrogen sulphide precipitates only copper sulphide from a slightly acidified solution containing copper and zinc ions, whereas if the filtrate is neutralized and made slightly alkaline with ammonia, hydrogen sulphide will now precipitate zinc sulphide.

The solubility of calcium sulphate in water at  $18^\circ\text{C}$ . is 0.015 gm. per litre. What is the value of its solubility product? Calculate how much calcium sulphate (in gm.-mol.) would be precipitated from a litre of its saturated solution if sodium sulphate were added to bring the total  $\text{SO}_4^{2-}$  concentration to 1.000 gm. ion per litre. (N.U.J.M.B.)

21. What is meant by the term "active mass" in relation to chemical reactions?

For the water-gas equilibrium at  $1000^\circ\text{Abs.}$ ,  $\text{H}_2\text{O} + \text{CO} \rightleftharpoons \text{H}_2 + \text{CO}_2$ , in which 8300 cal. are evolved, the equilibrium constant

$$\frac{p_{\text{H}_2} \cdot p_{\text{CO}_2}}{p_{\text{H}_2\text{O}} \cdot p_{\text{CO}}} = 3.24$$

A mixture of equal volumes of water vapour and carbon monoxide is allowed to reach equilibrium at  $1000^\circ\text{Abs.}$  at a total pressure of 1 atm. What is the final percentage composition by volume of the mixture?

(a) If the total pressure is altered to 0.1 atm. what will be the composition?

(b) If the temperature is raised, will there be more or less hydrogen in the equilibrium mixture?

Give appropriate explanations for (a) and (b). (N.U.J.M.B.)

## CHAPTER 19

1. Describe in detail how you would prepare (a) one lyophilic and (b) one lyophobic colloidal solution.

(What experiments would you use to show three essential differences in character between the two colloidal solutions whose preparation you describe? (O. & C.J.B.)

2. When hydrogen sulphide is passed into an aqueous solution of arsenious oxide, a yellow sol is produced. Describe the experiments that could be performed to investigate the nature of this sol, indicating clearly the purpose and principles of each experiment. (Inst. of Chem.)

3. How would you prepare colloidal solutions of (a) arsenic sulphide, (b) a metal such as gold or platinum?

Either describe a method by which the sign of the electrical charge on the particles of a colloid could be determined, or indicate briefly the part played by the electric charge in colloidal phenomena. (O. & C.J.B.)

4. Write an account of the factors involved in the stability of colloidal solutions. (Inst. of Chem.)

5. What are crystalloids and colloids? Give examples. Discuss some of the most important properties of colloids (Durham B.Sc.)

6. Give an account of the chief methods available for the preparation of a colloidal solution. What are the characteristics of such solutions. (London B.Sc.)

## CHAPTER 20

1. Write an essay on "Water: its occurrence and its chemical and physical properties." (N.U.J.M.B.)

2. How may a solution of hydrogen peroxide be prepared? Discuss its reactions with (a) an acidified solution of potassium permanganate, and (b) acidified potassium iodide solution. (Oxford Univ.)

3. What substances would you expect to find in natural water supplies? How would the content of the water vary with the location in which it was found? (Oxford Univ.)

4. Explain what is meant by hard and soft water. What tests enable you to distinguish between temporary and permanent hardness, and how is hardness removed from water? (Oxford Univ.)

5. Write an essay on the chemistry of hydrogen peroxide (Oxford Univ.)

6. How have very pure hydrogen and oxygen been prepared?

Describe, with a diagram of the apparatus, how the composition of water by weight has been accurately determined.

What is "conductivity water" and how is it prepared? (Oxford Locals)

7. Write an essay on the effects of intensive drying on physical and chemical properties. (London B.Sc.)

8. Indicate by means of equations four methods of preparing hydrogen. What weight of zinc is required to produce 100 litres of hydrogen gas measured at 27°C. and 680 mm pressure? (St Andrews Univ.)

9. How would you prove that the composition of water may be expressed by the formula  $H_2O$ ? Mention everything that this formula implies. What volume would 9 gm. of vapour occupy at 273°C. and 380 mm. pressure? (Aberdeen Univ.)

10. What are the chief properties of hydrogen peroxide? 20 c.c. of a solution of this substance after acidification with dilute hydrochloric acid, reduced 24 c.c. of 1/10 N potassium permanganate. Calculate the percentage of hydrogen peroxide in the solution. (St. Andrews Univ.)

11. What is meant by the terms temporary hardness and permanent hardness of natural water? How would you compare these? How would you treat a water for boiler purposes which contains substances producing both temporary and permanent hardness? (London B.Sc.)

12. How would you proceed in order to find the volumes in which hydrogen and oxygen combine to form water? What modification of your apparatus would you

make if you were asked in addition to measure the volume of steam formed? What volume of gas is formed when 72 grm. of water are decomposed, (a) electrolytically, (b) by means of sodium, (c) by heated iron? (Victoria Univ.)

13. What facts would you adduce to prove that the molecule of water contains two atoms of hydrogen and not more or less than two? (Science & Art Dept.)

14. How is hydrogen peroxide prepared? Mention any instances known to you of its action: (i) as an oxidizing agent, and (ii) as a reducing agent. What is the evidence that its molecule contains twice as much oxygen as a molecule of water? (London Univ.)

15. Describe the part played by calcium and magnesium salts in causing the hardness of water. How can the total hardness and the permanent hardness of a sample of water be determined?

If the solubility of carbon dioxide in water at 25°C. is 759 c.c. per litre (at one atmosphere pressure) what would be the maximum amount of calcium carbonate which one litre of water could dissolve under these conditions, assuming that all the carbon dioxide were converted to bicarbonate? (O. & C. J.B.)

## CHAPTER 21

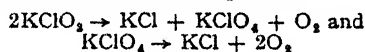
1. Give an account of the preparation and properties of ozone. How has the formula of ozone been determined. (Oxford Univ.)

2. Describe the preparation and principal properties of hydrogen peroxide.

"20 volume" hydrogen peroxide is a solution of hydrogen peroxide which liberates on decomposition twenty times its own volume of oxygen measured at N.T.P. If decomposition takes place according to the reaction  $2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2$ , calculate the concentration in grm per litre of a "20 volume" solution. (1 grm.-mol. wt. of a gas occupies 22.4 litres at N.T.P.) (O. & C. J.B.)

3. How would you prepare oxygen in a very pure state? Describe the action of oxygen on (a) hydrogen, (b) phosphorus, (c) sodium. (Oxford Univ.)

4. There are reasons to believe that the equations:



do not actually represent the decomposition of potassium chlorate when heated. Describe the experiments you would make in order to test the validity of these equations. (New Zealand Univ.)

5. Outline the chemistry of the hydrides. How far can they be grouped into types? (Oxford Scholarships.)

6. What is the difference between "a neutral oxide" and "an amphoteric oxide"? Discuss the chemistry of any element which forms a neutral oxide. (Oxford Scholarships)

7. Write an account of the chemistry of ozone. In what way is the composition of ozone deduced? (St. Andrews Univ.)

8. Classify the following oxides, justifying your classification by a concise description of the properties of each. antimonous oxide, bismuth oxide, aluminium oxide, chromium sesquioxide, sodium peroxide. (Oxford Univ.)

9. Describe the preparation and properties of ozone. How was the composition of ozone ascertained? How does ozone react with (a) mercury, (b) finely divided silver, (c) a solution of potassium iodide? What occurs when ozonized oxygen is strongly heated and cooled? (London Inter. B.Sc.)

## CHAPTER 22

1. What do you understand by (a) combustion, (b) explosion? Give examples to illustrate the principal features of these phenomena. (O. & C. J.B.)

2. How would you prepare carbon monoxide in the laboratory? How is it obtained on a commercial scale? What is its action on (a) ferric oxide, (b) nickel, (c) chlorine?

Mention the conditions necessary for chemical reaction in each case. (London Inter. B.Sc.)

3. Explain how the quantitative and qualitative composition of carbon dioxide and carbon monoxide have been ascertained. (St. Andrews Univ.)

4. Give an account of the manufacture and purification of coal gas. What are the principal constituents of the gas supplied to houses for domestic use?

5. 10 c.c. of a gaseous hydrocarbon are exploded with an excess of oxygen. A contraction of 15 c.c. is observed. After the explosion, a contraction of 20 c.c. is observed on treating the resulting gases with potassium hydroxide solution. What is the molecular formula of the hydrocarbon?

6. How do you account for the fact that in spite of the large amount of oxygen consumed in respiration and combustion, the percentage of oxygen in the atmosphere remains practically unaltered? (Manchester Univ.)

7. Give the chief chemical and physical properties of  $\text{CO}_2$  and  $\text{CS}_2$ . (Manchester Univ.)

8. Describe the properties of carbon which tend to show that diamonds could not have been formed at a temperature at which pure iron melts. How would you show that carbon dioxide is a compound of carbon and oxygen, and that it contains very nearly its own volume of oxygen? (London Univ.)

9. What is charcoal, and how can it be made on a large scale? Describe the differences between peat, lignite, bituminous coal, anthracite, and graphite. (Bombay Univ.)

10. Describe the construction of a Davy lamp, and indicate the principles on which its action as a safety lamp depends. (London Univ.)

11. Give three reasons for the non-luminosity of the flame of a bunsen burner. When will such a flame strike back? What causes the luminosity of an ordinary gas flame? Why does the amount of carbon dioxide in the atmosphere remain practically the same? (Cornell Univ.)

12. Describe and comment on the experiments which serve to elucidate the nature of flame. (Durham Inter. B.Sc.)

## CHAPTER 23

1. Give an account of the processes used in the fixation of atmospheric nitrogen. (Oxford Univ.)

2. Give illustrations of the behaviour of different metals towards nitric acid. (Aberdeen Univ.)

3. What is observed, and what products are obtained, when each of the following nitrates is heated until any decomposition which occurs is complete: copper nitrate, mercuric nitrate, ammonium nitrate, sodium nitrate? How would nitrogen be isolated from one of these nitrates? (Sheffield Univ.)

4. Under what conditions and with what results does nitrogen combine with (a) hydrogen, (b) oxygen, (c) magnesium, (d) calcium carbide? (London B.Sc.)

5. How would you prove that nitric acid acts both as an oxidizing and as a reducing agent? (London Univ.)

6. What is the action of concentrated nitric acid on tin, iodine, and sulphurous acid solution? (St. Andrews Univ.)

7. Why are the compounds formed by the union of acids with ammonia termed ammonium compounds? Quote facts which may be regarded as evidence that a solution of ammonia in water contains ammonium hydroxide. (London Univ.)

8. Outline the usual laboratory preparation of (a) nitrous oxide, (b) nitric oxide. Compare the reactions (if any) of carbon, sulphur, and phosphorus with these gases and state the reasons why the two gases behave rather differently.

How would you (i) obtain nitric oxide from a mixture of nitric and nitrous oxides, (ii) show that nitric oxide is an oxide of nitrogen? (N.U.J.M.B.)

9. Explain or comment on the following:

(a) Some metals which are not normally soluble in dilute acids dissolve in dilute nitric acid.

(b) Some metals which dissolve in dilute nitric acid become insoluble in other dilute acids after treatment with concentrated nitric acid.

(c) Some sulphides which are precipitated in dilute acid solution will re-dissolve in dilute nitric acid.

(d) A convenient way of removing nitric acid from a solution is to add ammonium hydroxide until the solution is just alkaline and then boil the solution for some time. (O. & C.J.B.)

10. Describe the manufacture of nitric acid. What products may be obtained by the action of heat upon nitrates? (Oxford Univ.)

11. How would you obtain a specimen of nitrogen tetroxide as pure as possible? Give an account of its properties and explain the changes it undergoes on heating. (Oxford Univ.)

12. Give an account of the reactions that can take place between nitrogen and the following substances, mentioning the necessary conditions: hydrogen; oxygen; calcium carbide; magnesium. (Oxford Univ.)

13. *Either*, Describe in outline *one* method for the manufacture of nitric acid. How is silver nitrate used in (a) qualitative and (b) volumetric analysis?

*Or*, Describe briefly how you would prepare *two* of the oxides of nitrogen from nitric acid. Compare the properties of nitric oxide and nitrogen peroxide with regard to their reactions with (a) water, (b) alkalis, (c) oxidizing and reducing agents. (O. & C.J.B.)

14. Review the inorganic chemistry of nitrogen; comment briefly on the compounds which nitrogen forms with sulphur and with oxygen. (Inst. of Chem.)

15. Describe the industrial production of substances using common salt, air, water, and limestone (or chalk) as raw materials. (Oxford Scholarships.)

16. Outline the steps by which you could obtain samples of hydrogen, oxygen and nitrogen from nitric acid.

How and under what conditions does nitric acid react with (a) copper, (b) zinc, (c) phosphorus? In (a) and (b) what property of the metal principally determines the difference in reaction? (N.U.J.M.B.)

17. What method would you use in the laboratory to prepare a specimen of nitrogen? (No experimental details are required.)

Give an example of (a) a metal, (b) a non-metal, (c) a compound, which combines directly with nitrogen, stating the conditions and products in each case. Describe the action of water on the products obtained in (a), (b), and (c). (Cambridge Locals.)

18. Describe how, starting with nitric acid, you would obtain specimens of (a) lead nitrate, (b) ammonia, (c) nitrous oxide, (d) nitric oxide.

What reactions occur when the compounds (a), (b), and (c) are heated? (Cambridge Locals.)

## CHAPTER 24

1. What is the fundamental reaction of the contact process for the manufacture of sulphuric acid?

Discuss the conditions necessary to obtain a maximum yield in this fundamental reaction.

Starting from commercial sulphur state how you would obtain (a) crystals of rhombic sulphur, (b) sodium sulphate, (c) sodium thiosulphate. (N.U.J.M.B.)

2. Compare and contrast the properties of sulphur dioxide and sulphur trioxide, and of the acids which can be formed from them. (O. & C.J.B.)

3. Write a brief account of the allotropy of sulphur. Starting from elementary sulphur how would you prepare (a) sodium thiosulphate, (b) sodium persulphate? Describe the properties of these two salts.

4. Briefly discuss the essential conditions and reactions governing the conversion of sulphur dioxide to sulphuric acid by the contact process.

Show by its reactions with *one* substance in each case that sulphuric acid can act (a) as an oxidizing agent, (b) as a dehydrating agent.

Write equations for the reaction between concentrated sulphuric acid and

(c) potassium chloride, (d) potassium bromide, (e) a mixture of sodium chloride and manganese dioxide. (N.U.J.M.B.)

5. Liebig declared that a nation's industrial pre-eminence may be measured by its consumption of sulphuric acid. Justify this statement by:

(a) discussing briefly the acid nature, acid strength, high boiling point, affinity for water and oxidizing power of sulphuric acid;

(b) describing its use (i) in the fertilizer industry, (ii) in any two of the following: plastics, dyes, rayon, galvanizing, chemicals, woollen textiles. (N.U.J.M.B.)

6. Explain carefully the reasons for assigning to sulphur dioxide the formula  $\text{SO}_2$ . (Oxford Scholarships.)

7. Discuss with the help of graphical methods of representation the equilibria between the different forms of sulphur (London B.Sc.)

8. Describe as fully as possible from your own laboratory experiments the chemistry of the compounds of sulphur. (Durham B.Sc.)

9. What do you know regarding the general behaviour of metallic sulphides towards (a) water, (b) hydrochloric acid, (c) caustic soda? Give equations. (St. Andrews Univ.)

10. Explain the reaction involved in the production of sulphuric acid in the "Chamber Process" and give the means adopted to prevent the escape of nitrous gases into the atmosphere. Give two illustrations of the use of sulphuric acid as (a) a dehydrating agent, (b) an oxidizing agent. (Sheffield Univ.)

11. Describe the occurrence of sulphur in nature. Given crude sulphur containing calcium sulphate and sand, how could you prepare a pure specimen of the element, and what tests would you apply to demonstrate its purity?

Indicate precisely the reactions involved in preparing a specimen of sodium thiosulphate from sulphur and caustic soda. (Durham B.Sc.)

12. How does sulphur occur in nature, and how is it obtained as stick sulphur and flowers of sulphur? Describe the changes which sulphur undergoes when heated and give some account of its allotropic forms (New Zealand Univ.)

13. Give an account of the occurrence of the element sulphur and its compounds in nature. Describe the preparation and properties of the various modifications of sulphur. (St. Andrews Univ.)

14. What happens on heating with sulphuric acid, (a) manganese dioxide, (b) cuprous oxide; with nitric acid, (a) black oxide of iron, (b) red lead; with hydrochloric acid, (a) red oxide of iron, (b) black oxide of manganese? (London Univ.)

15. Discuss the ways in which sulphur atoms combine in the various physical forms in which sulphur can exist. Mention some inorganic compounds of sulphur which contain at least one S—S bond, and describe their properties. (Inst. of Chem.)

16. Discuss the principles underlying the use of hydrogen sulphide as a reagent in qualitative analysis.

The solubility of silver sulphide is  $1.24 \times 10^{-14}$  gram. per litre at  $25^\circ$ . Calculate its solubility product at this temperature. (Cambridge Locals.)

## CHAPTER 25

1. Write an essay on "Interhalogen compounds." (Inst. of Chem.)

2. Write a short account of the chemistry of the compounds of fluorine with (a) oxygen, and (b) the other halogens. (Inst. of Chem.)

3. How does fluorine occur naturally and how may it be isolated? Summarize the main points of the chemistry of this element which justify placing it in the halogen group. (Inst. of Chem.)

4. Write explanatory notes upon the following reactions and show how they illustrate the general chemistry of iodine:

(a) Iodine and sulphurous acid,

(b) Sodium iodide and nitrous acid,

(c) Iodine and aqueous sodium hydroxide,

(d) Iodine and aqueous sodium iodide,

(e) Iodine and concentrated nitric acid. (Durham Inter B.Sc.)

5. Outline the methods by which the halogens can be isolated from their compounds and with the aid of a tabular statement of the formulae and properties of their compounds indicate, (a) why the halogens are regarded as a family of related elements, and (b) what important differences exist among them. (Durham B.Sc.)

6. Describe and explain the behaviour of an aqueous solution of chlorine, (a) when exposed to sunlight, (b) when distilled, (c) when added to a cold solution of sodium hydroxide, (d) when added to a suspension of chalk, (e) when added to a suspension of yellow mercuric oxide. (London Inter. B.Sc.)

7. Explain the method for extracting iodine from the mother liquors of Chile saltpetre manufacture. What action has each of the following substances upon the element: nitric acid, chlorine, potassium chlorate, sulphurous acid? Specify the conditions needed for each of the reactions given. (London Inter. B.Sc.)

8. Discuss compounds of positive iodine. On the basis of the increase in positive character of the halogens with increasing atomic weight, describe the properties which you would expect astatine to possess. (Inst. of Chem.)

9. Write an account of the isolation and chemistry of bromine. (Oxford Univ.)

10. Give an account of the preparation of hydrogen iodide. Compare and contrast the properties of hydrogen iodide with those of hydrogen chloride. (Oxford Univ.)

11. Describe with a diagram how you would prepare and collect several gas-jars full of chlorine using common salt as its source.

What is the action of chlorine on (a) water, (b) sodium hydroxide solution, (c) hydrogen sulphide? Give equations. (Oxford Univ.)

12. Compare and contrast the chemistry of chlorine and iodine.

Describe *two* tests by which you would distinguish a sample of potassium iodate from one of potassium chlorate (Cambridge Locals.)

13. Outline the preparation and properties of the oxides of fluorine, bromine, and iodine. Adduce evidence to support the statement that iodine exhibits basic properties not shown by the other halogens. (Inst. of Chem.)

14. Tabulate the oxygen compounds of the halogens and write notes on those which are remarkable either for theoretical interest or practical importance. (Inst. of Chem.)

15. Which, do you think, is the most interesting element in Group VII of the Periodic Table? Give your reasons. (Oxford Scholarships.)

16. Why was fluorine regarded as an element and classed with the halogens before it had been isolated? Give a brief account of its chemical and physical properties. (London Inter. B.Sc.)

17. Show how fluorine differs in chemical behaviour from the other halogens, and give any explanation you can of its abnormality. (Durham B.Sc.)

18. Give an account of the oxides and oxyacids of the halogens. (Durham Inter. B.Sc.)

19. Describe how potassium iodate can be made from iodine.

Give an account of the principal properties and uses of the chlorates and iodates of sodium and potassium.

Comment on the statement: Iodine displaces chlorine in compounds which also contain oxygen. (O. & C.J.B.)

20. What reactions can take place between the following pairs of substances, and under what conditions will the reactions occur:

- (a) sodium iodate (e.g., in caliche) and sodium bisulphite;
- (b) iodine and sodium thiosulphate;
- (c) copper sulphate and potassium iodide?

Explain the importance of these reactions. (O. & C.J.B.)

21. What are the main sources of iodine? Describe the preparation of iodine from these sources. What is the action of iodine with *four* of the following: chlorine; sodium arsenite; sodium thiosulphate; nitric acid; aqueous ammonia? (Oxford Univ.)

22. Write an essay on the chemistry of fluorine (Inst. of Chem.)

23. How is fluorine isolated? In what ways does the chemistry of this element differ from that of the other halogens? How far can these differences be accounted for? (Oxford Univ.)

24. Describe the isolation and purification of iodine from natural sources. Give an account of the uses of iodine and its compounds in volumetric analysis. (Oxford Univ.)

25. Contrast the methods by which hydrochloric acid gas and hydriodic acid gas (hydrogen chloride and hydrogen iodide) are usually made in the laboratory. How do you account for the differences?

Give equations for the reactions which take place between potassium iodide and (a) an acidified solution of potassium iodate, and (b) a solution of mercuric chloride. State the uses to which these reactions can be put in the laboratory. (Oxford Univ.)

26. What do you know of the discovery, manufacture, properties, and uses of fluorine? Discuss the chemical differences between fluorine and chlorine. (Oxford Locals.)

27. Describe the preparation of potassium iodate in a state of purity and summarize the uses to which it can be put in volumetric analysis

28. Starting in each case with iodine, describe how you would prepare (a) iodic acid, (b) potassium iodate.

How would you (i) obtain iodine pentoxide from (a), (ii) use (b) to prepare a decinormal solution of iodine?

Compare the properties of iodic acid and potassium iodate with those of chloric acid and potassium chlorate. (Oxford Locals.)

29. Name the main source of bromine, and describe briefly how the element may be extracted from it. Discuss the reactions which take place between bromine and each of the following: (a) hydrogen sulphide, (b) aqueous sulphur dioxide, (c) sodium hydroxide, (d) ethylene. (Cambridge Locals.)

#### CHAPTER 26

1. How would you remove the chemically active constituents of air in order to show that part of it is inert? What part did the discovery of the inert gases play in the development of modern chemical ideas? (O. & C.] B.)

2. Discuss briefly the importance of the rare gases in the development of chemical ideas.

The density of solid argon is 1.65 grm/ml. Derive a rough value for Avogadro's number, taking the atomic weight of argon to be 40, and the diameter of an argon atom to be  $3.2 \times 10^{-8}$  cm. (Oxford Scholarships.)

3. Give an account of the discovery of the inert gases, and the part they have played in the discovery of the classification of the elements. (London Inter. B.Sc.)

4. A given volume of air is left in contact with lime (calcium oxide); a second volume of air is shaken up with acidified solution of ferrous sulphate. Carefully describe the changes which occur in the air and in the reagent in each case. (Univ. North Wales.)

5. Discuss the position of the helium family in the Periodic Classification. (St. Andrews Univ.)

6. Name the gases which form the atmosphere and describe the part which each plays in connection with animal and vegetable life. (Tasmania Univ.)

7. Describe experiments by means of which the composition of air may be determined. On what evidence is it concluded that the air is a mixture and not a compound?

#### CHAPTER 27

1. Give an account of the occurrence of metals and of the general methods of obtaining them from their ores, illustrating your answer by reference to the extraction of aluminium, chromium, iron, lead, mercury and tin. (Oxford Locals.)

2. Describe methods which may be used for the extraction of the alkali and



alkaline earth metals from their salts. Emphasis should be placed on the chemical principles underlying the methods rather than on technical details of processes. (Inst. of Chem.)

3. Classify and give examples of the reactions which occur between metals and mineral acids under various conditions. (Oxford Scholarships.)

4. "Light metals" are now used in many industries. Give examples of such metals and outline the methods used in their production from natural sources. What merits or disadvantages have these metals in comparison with steel? (Oxford Scholarships.)

5. Give an account of the occurrence of the ores of the common commercial metals, classifying them according to their chemical nature and indicating briefly the principles upon which selection of a particular ore for smelting depends.

6. Summarize the methods which are applied to the concentration of metallic ores in preparation for the extraction of the metal from them and describe their application to the case of one common metal.

## CHAPTER 28

1. You are provided with a dry mixture of the pure substances (a) anhydrous sodium carbonate, (b) potassium chloride and (c) anhydrous sodium sulphate.

Describe briefly the analytical experiments you would make in order to find the *quantitative* composition of the mixture. Show how you would use your analytical data to calculate the amount of each component in the mixture. (Choose the minimum number of experiments necessary to find the composition of the mixture.) (N.U.J.M.B.)

2. Describe the properties, uses and structures of (a) sodium peroxide, (b) sodium azide, (c) sodium cyanide. It has recently been suggested that the yellow colour of technical sodium peroxide is due to the presence of a few per cent of sodium superoxide,  $\text{NaO}_2$ . How would you attempt to confirm this suggestion? (Inst. of Chem.)

3. Mention two commercial uses of sodium hydroxide.

Describe briefly, giving a diagram, an electrolytic method by which sodium hydroxide is manufactured.

Under what conditions and with what results does sodium hydroxide react with (a) chlorine, (b) carbon monoxide, (c) silica? (N.U.J.M.B.)

4. Outline the procedure and reactions involved in the Solvay (ammonia-soda) process for the manufacture of sodium carbonate.

Describe and briefly explain *one* use of sodium carbonate in qualitative analysis.

Explain briefly why calcium hydroxide is used for the detection of carbon dioxide gas whereas potassium hydroxide is used for the absorption of the gas. (N.U.J.M.B.)

5. Describe and explain a process for the manufacture of sodium hydroxide.

What substances can be obtained by the action of chlorine on aqueous sodium hydroxide? Give equations. (Oxford Univ.)

6. How are (a) sodium carbonate, (b) sodium hydroxide obtained? Outline the chemistry and uses of *one* of these compounds. (Oxford Univ.)

7. Describe the Solvay ammonia-soda process for making sodium carbonate from sodium chloride. Why should there be such a great demand for sodium carbonate? (London Inter B.Sc.)

8. What is the chief natural source of potassium? Describe how pure potassium chloride is obtained therefrom and how this material is subsequently converted into potassium carbonate.

9. Contrast the chemical properties of potassium with those of sodium. (Durham B.Sc.)

10. From what minerals are the salts of potassium prepared and where do they occur? How is potassium nitrate prepared from potassium chloride? How would you show the presence of potassium in the presence of a mixture of calcium, sodium, and potassium chlorides? (Aberdeen Univ.)

## CHAPTER 29

1. Give an account of the extraction of silver (a) from its sulphide ore, (b) from an alloy of lead and silver.

What do you know concerning the use of silver nitrate (i) in volumetric analysis; (ii) in the detection of acid radicals? (Oxford Locals.)

2. Give an account of the chemistry of silver and its compounds, and explain how anions in solution can be distinguished by the use of silver nitrate in conjunction with certain other reagents.

3. How is copper obtained from its ores? Summarize briefly the reactions of copper with the common inorganic acids. (Oxford Univ.)

4. Give a general account of the chemistry of *either* cobalt *or* nickel. (Oxford Univ.)

5. Describe the successive phenomena observed when ammonium hydroxide solution is added drop by drop to a solution of cupric sulphate and indicate by formulae or equations the nature of the changes that occur (Massachusetts Polytech.)

6. (a) Show the analogy between the reactions of copper on nitric acid and copper on sulphuric acid. (b) What products are formed when the concentrated sulphuric acid is warmed with potassium iodide? (c) What reasons have you for thinking that no nascent hydrogen is formed in the reactions mentioned under (a)? (Amherst Coll., U.S.A.)

7. Give an account of the chemistry of silver and its compounds. Contrast the behaviour of silver with that of other metals forming monovalent cations. (Oxford Univ.)

8. (a) In the laboratory you passed dry hydrogen over copper oxide which was heated in a tube. How does this experiment illustrate: a synthetic reaction, an analytical reaction; oxidation and reduction?

(b) If you started with an unknown mixture of copper oxide and copper, say 10 grm., and after heating and passing hydrogen over it, the resulting weight of pure copper was 9.2 grm., how much of the original weight of the mixture was copper oxide and how much was metallic copper? (Worcester Polytech., U.S.A.)

9. Illustrate, and explain, the fact that the chemistry of silver differs from that of copper and sodium. (Oxford Scholarships.)

10. Show how the chemistry of copper, silver and gold may be correlated on the basis of the electronic structures of these elements. (Inst. of Chem.)

## CHAPTER 30

1. Write an account of the chemistry of barium and explain the principles involved in the differentiation between calcium, strontium, and barium in qualitative analysis. (Oxford Univ.)

2. How is magnesium obtained on a large scale?

Starting from magnesium how would you prepare (a) anhydrous magnesium chloride, (b) magnesium oxide, (c) magnesium hydroxide? (Cambridge Locals.)

3. Describe the main chemical properties of magnesium, barium, and mercury and comment on the relationship of these elements. (Oxford Scholarships.)

4. Compare the chemistry of magnesium with that of (a) calcium and (b) zinc. (Oxford Scholarships.)

5. What is quick-lime? How is it obtained? What takes place (a) when lime is mixed with water? (b) when it is heated strongly with sand? (c) when it is exposed to carbon dioxide gas? Give equations. (Aberdeen Univ.)

6. How does calcium occur in nature? What are its principal compounds in everyday use, and how are they made from naturally occurring compounds? How is metallic calcium made? Give the formulae of the typical salts of calcium and the ions formed on solution of these salts in water. (Sydney Univ.)

7. Briefly describe the chief properties of the metal calcium. In what way and under what conditions does slaked lime react with (a) sodium carbonate, (b) chlorine, (c) ferric chloride, (d) sulphur? (London Inter, B.Sc.)

8. Give the names and formulae of the four principal minerals containing calcium. How is metallic calcium prepared? By what reaction would it be possible to prepare from the metal specimens of (a) calcium hydroxide, (b) calcium carbonate, (c) bleaching powder? (London Univ.)

### CHAPTER 31

1. Compare and contrast the chemistry of the elements magnesium, zinc and mercury, and of their commoner compounds. (Oxford Locals)

2. Compare and contrast the chemistry of zinc with that of mercury. (Oxford Univ.)

3. Give an account of the chemistry of mercury and its compounds, emphasizing any similarities to other elements. (Oxford Univ.)

4. How does mercury occur in nature and how is it obtained from its ores? How would you prepare chemically pure mercury from a commercial specimen? (London Inter. B.Sc.)

5. How can mercuric and mercurous chloride be obtained from mercuric sulphate? What is the action of mercuric chloride solution with solutions of (a) potassium iodide, (b) stannous chloride, (c) ammonia, (d) sodium hydroxide? (London Univ.)

6. Compare the chemical properties of the elements zinc, cadmium, and mercury and their chief compounds. (Oxford Univ.)

7. What are the chief ores of zinc? Describe in detail the extraction of the metal from one of these ores, and indicate the industrial applications of zinc and its compounds. (London B.Sc.)

8. Describe the occurrence, isolation, and properties of the metal cadmium. Show that in chemical behaviour cadmium resembles zinc and mercury. (London B.Sc.)

9. Mercury forms two classes of salts—mercurous and mercuric salts. Illustrate by examples how these salts differ in composition from each other. How would you discover whether a given mercury salt was mercurous or mercuric salt? (London Univ.)

10. Give an account of the metal mercury and its behaviour towards the common acids. Give the formulae and the names (systematic and trivial) of its chief compounds. (London Univ.)

11. Name the principal ores of zinc and describe the production of the pure metal from these ores. How does zinc react with (a) a solution of sulphur dioxide, (b) dilute sulphuric acid, (c) a solution of copper sulphate, (d) dilute nitric acid?

### CHAPTER 32

1. Give an account of the compounds of hydrogen and boron. (Inst. of Chem.)

2. Describe the isolation of aluminium from its ores. Write a general account of the chemistry of aluminium. (Oxford Univ.)

3. Boron trichloride contains 90.77 per cent of chlorine and its vapour density is 58.6. Calculate the atomic weight of boron.

The vapour density of a volatile boron hydride is 13.8. When 0.0691 g. of this hydride was added to water a solution of orthoboric acid was formed and hydrogen gas was evolved which occupied (when dry) a volume of 374.2 ml. at 27° C. and 750 mm. pressure. Deduce the formula for the volatile hydride and write down the equation for its reaction with water. (Oxford Univ.)

4. Give an account of the chemistry of gallium, indium, and thallium, illustrating the importance of the inert-pair effect. (Inst. of Chem.)

5. How is metallic aluminium obtained? How would you prepare from it the anhydrous chloride? Why cannot this substance be obtained when an aqueous solution of aluminium oxide in hydrochloric acid is evaporated to dryness and the residue ignited? (London Inter. B.Sc.)

6. Describe briefly the chemical characteristics of boron and its compounds.

Discuss the relationship of this element to (a) aluminium, (b) silicon. (London Univ.)

7. Explain how a high temperature is obtained in the "aluminothermic" processes, and why so much heat can be made effective as compared with many other processes of combustion. (Worcester Poly. Inst., U.S.A.)

8. Describe in detail the production of aluminium and indicate the various uses to which the metal is now put. (London Inter. B.Sc.)

9. How does aluminium react with three of the following: (a) hydrochloric acid, (b) nitric acid, (c) sodium hydroxide, (d) ferric oxide, (e) the atmosphere? Specify the conditions needed for the reactions you mention. (London Inter. B.Sc.)

10. What is the composition of borax and to what class of salts does it belong? Mention some examples of other salts of similar composition. What is the action of a solution of borax on litmus? (London Univ.)

11. Write the formulae of the chief "alums" known. Point out their characters as a class. State and explain the principle they illustrate. (London Univ.)

### CHAPTER 33

1. What is the "lanthanide contraction"? Discuss its effects on the properties of elements outside the rare-earth series. Give an account of the various methods which have been used for separating the rare earths, paying particular attention to the underlying principles. (Inst. of Chem.)

### CHAPTER 34

1. The elements carbon, silicon and tin fall in the same group of the Periodic Table. How far are their properties in harmony with this common grouping? (London B.Sc.)

2. How would you proceed to prepare from litharge specimens of red lead and lead dioxide? Give details of the experimental procedure and describe precisely how you would estimate the percentage of metal in either of the above materials. (Durham B.Sc.)

3. Write concise but full notes on the silicic acids and the silicates. (Durham B.Sc.)

4. Describe with special reference to the reactions involved the preparation of pure lead from galena and of the several oxides from the metal. Give a brief account of the properties and uses of these oxides. (Durham B.Sc.)

5. Describe the process of extracting tin from its ores. What are the properties to which the usefulness of tin is due? How may (a) stannic oxide, (b) stannic chloride, (c) sodium stannate, be obtained from the metal? (London Inter. B.Sc.)

6. How can (a) silicon, and (b) silicon carbide be obtained from sand, and for what purposes are these substances used? How can silicon chloride be obtained from silica, and converted into silica? (Sheffield Univ.)

7. Give an account of the element silicon. Discuss the classification of the silicates. (Cape Univ.)

8. What would be produced if tin foil were introduced into solutions of the following salts: silver nitrate, lead acetate, copper sulphate, copper chloride, stannous chloride, alum, ferric chloride? Give equations. (London Univ.)

9. Write a comparative account of the chemistry of carbon and silicon. How are the following facts accounted for: (i) carbon dioxide is a gas whereas silica is a solid of very high melting point; (ii) carbon tetrachloride is unaffected by water whereas silicon tetrachloride is readily hydrolysed by water?

10. Give the names and formulae of the oxides of lead, and describe all that can be observed when each of these oxides is heated in an open crucible. From 1 gram. of one of the oxides of lead, 1.269 gram. of lead sulphate can be obtained; which of the oxides is it? (Sheffield Univ.)

11. Write a comparative account of the chemistry of silicon, tin, and lead. (Oxford Scholarships.)

12. Starting from red lead ( $\text{Pb}_3\text{O}_4$ ), describe in detail how you would prepare samples of lead nitrate, lead peroxide, lead iodide, and litharge ( $\text{PbO}$ ). (Oxford Univ.)

13. What is the chief ore of lead? How is the metal extracted from this ore? Describe how the following lead compounds can be obtained from the metal: (a) the nitrate; (b) the dioxide; (c) white lead.

Give *two* tests by which you could distinguish between lead chloride and mercurous chloride. (Oxford Locals)

14. Compare and contrast the properties of the oxides of carbon, silicon, tin and lead. Comment on the nature of the bonds in the oxides of carbon and silicon. (Cambridge Locals.)

15. Compare the properties of silicon and lead and the properties of their simple derivatives. Why is lead classed as a metal and silicon as a non-metal? (Oxford Univ.)

16. Name *one* common ore of tin, and describe *briefly* how the metal may be extracted from it.

With tin as starting material, how would you prepare a sample of (a) stannic chloride, (b) stannous sulphide?

25 ml. of a solution of stannous chloride in dilute hydrochloric acid are found on titration to be equivalent to 20.4 ml. of decinormal iodine solution. What is the weight of tin in 1 litre of the solution? ( $\text{Sn} = 119$ .) (Cambridge Locals.)

17. Illustrate by examples the existence of divalency in the elements carbon, tin, and lead. Comment on the difference between these elements in the divalent state with special reference to oxides and chlorides. (O. & C.J.B.)

18. How may silica be obtained in a pure state from sand? How may silicon be obtained from silica? How would you prepare (a) silicon tetrachloride, (b) silicon tetrafluoride from silica? (London Inter. B.Sc.)

19. Describe the preparation, properties and reactions of the compounds of silicon with hydrogen, with chlorine, and with fluorine. (Aberdeen Univ.)

20. Compare and contrast the elements carbon and silicon by a discussion of their analogous inorganic compounds. (Sheffield Univ.)

## CHAPTER 35

1. Compare, in the light of the Periodic Table, the properties of the elements arsenic, antimony, and bismuth and their compounds. (Oxford Univ.)

2. Describe a process for the manufacture of chlorine. What are its industrial uses? (Oxford Univ.)

3. Give an account of the chemistry of the oxyacids of phosphorus, referring where possible to structure, preparation and typical properties. (Inst. of Chem.)

4. Give an account of the preparation and properties of metallic arsenic, arsine, arsenious oxide and arsenates. (Oxford Univ.)

5. How are phosphorus trichloride and phosphorus pentachloride made? What explanation has been offered of the fact that the vapour density of phosphorus pentachloride is 52.2 at  $350^\circ$  and what experimental evidence has been adduced in support of this explanation?

6. How are phosphorus trioxide and phosphorus pentoxide respectively prepared? What happens when phosphorus pentoxide is dissolved in cold water and then the solution is boiled? What is the action of heat on orthophosphoric acid? (Aberdeen Univ.)

7. Compare the hydrides of nitrogen, phosphorus, arsenic, and antimony. (Univ. Pennsylvania.)

8. In what forms does arsenic occur in nature? How is the element obtained? How may (a) arsenic trichloride, (b) arsenic trioxide and (c) arsenic acid be prepared? What methods are available for the detection of arsenic in small amounts?

9. Give an account of the oxyacids of phosphorus and their salts, indicating those which have industrial applications. (Oxford Univ.)

10. Describe how the law of mass action can be applied to the dissociation of

phosphorus pentachloride, both by itself and in the presence of chlorine gas, and state and explain what influence change of pressure and temperature have on this dissociation. (Madras Univ.)

11. How may the different modifications of phosphoric acid be obtained, and by what tests may they be distinguished? (Aberdeen Univ.)

12. Describe carefully the preparation of the gaseous hydride of phosphorus and compare its properties with those of the corresponding hydrides of nitrogen and arsenic. (Sheffield Univ.)

13. What is the evidence for the existence of antimonyl and bismuthyl compounds? Describe the preparation of an antimonyl compound from antimony, and of a bismuthyl compound from bismuth; give briefly the properties of each; and explain the reactions that occur when each is boiled with sodium carbonate solution. (Punjab Univ.)

14. Compare the properties and methods of preparation of the hydrides of nitrogen, phosphorus, arsenic, antimony and bismuth. (London B.Sc.)

15. Describe the isolation of elementary phosphorus from its ores. Explain how the two allotropes of phosphorus may be interconverted and outline any important differences in the chemical reactions of the two allotropes. (Oxford Univ.)

16. Describe the industrial preparation of white (yellow) phosphorus. How would you prepare it from (a) phosphine, (b) phosphorus pentachloride, (c) phosphorous pentoxide? (Cambridge Locals.)

17. Describe, with a diagram of the apparatus, how you would prepare phosphorus trichloride, stating the precautions necessary to obtain a reasonably pure product.

How does phosphorus pentachloride react with (a) water, (b) phenol?

The vapour density of phosphorus pentachloride at  $200^{\circ}\text{C}$ . is 70; theoretically it should be 104.3. How do you explain this anomaly and what can you deduce from the facts given? (Oxford Locals.)

18. Compare and contrast the physical and chemical properties of white and red phosphorus.

Given solutions of orthophosphoric acid and sodium hydroxide, describe how you would prepare specimens of the three sodium phosphates. What is the action of heat on each of these salts? (Oxford Locals.)

19. Compare and contrast the properties of the hydrides, oxides, and halides of nitrogen, phosphorus, and arsenic. (Oxford Univ.)

20. Give an account of the isolation of arsenic. Outline the chemical reactions of the element and its compounds. How are small quantities of arsenic detected? (Oxford Univ.)

21. Write an essay on the oxyacids of phosphorus. What tests distinguish between ortho-, meta-, and pyro-phosphoric acids? (Oxford Univ.)

22. Compare and contrast the properties of (a) the trichlorides  $\text{XCl}_3$  and (b) the trioxides  $\text{X}_2\text{O}_3$  where X is phosphorus, arsenic or antimony. (O. & C.J.B.)

## CHAPTER 37

1. Give a careful account of the chemistry of the less common elements of the Sixth Group of the Periodic Table and compare and contrast them with other elements in that part of the Table. (Durham B.Sc.)

2. Starting in each case with potassium dichromate describe the preparation of (a) chromic anhydride, (b) chromium sesquioxide, (c) chrome alum, (d) chromyl chloride, (e) potassium chromate. (London Inter. B.Sc.)

3. Compare and contrast the main features of the chemistry of chromium, molybdenum, and tungsten.

A solution of ammonium molybdate containing 0.0720 g. of molybdenum was reduced with zinc amalgam and hydrochloric acid, and the resulting solution was found to be equivalent to 22.5 ml. of 0.1 N ceric sulphate. To what oxidation state had the molybdenum been reduced? ( $\text{Mo} = 96.0$ ). (Inst. of Chem.)

4. The oxide of chromium  $\text{Cr}_2\text{O}_3$ , and the hydroxide,  $\text{Cr}(\text{OH})_3$ , are weakly basic and still more weakly acidic. How does this statement accord with the fact that the salt  $\text{Cr}_2(\text{SO}_4)_3$  is stable in water while the corresponding carbonate and sulphide are not stable? What compound is formed when sodium carbonate is added to a solution of a chromic salt? (Massachusetts Inst. Technology.)

5. What happens when sodium hydroxide is mixed with a solution of a chromic salt? Of a potassium chromate solution? Of a potassium dichromate solution? Give four reactions which distinguish chromium from all other elements. (Amherst Coll., U.S.A.)

### CHAPTER 38

1. Illustrate the chief characteristics of the transition series of elements (Cr to Cu) by reference in detail to the chemistry of manganese. (Oxford Univ.)

2. How is manganese extracted from its ores? Describe the preparation of potassium permanganate, and indicate its usefulness in volumetric analysis. (Oxford Univ.)

3. Show how the chemistry of manganese can be correlated with its position in the Periodic Table, and point out any features by which it is distinguished from neighbouring elements. (Oxford Univ.)

### CHAPTER 39

1. Describe the manufacture of pig-iron from an ore of iron, paying attention to the essential functions of the materials involved and to the reactions which occur.

State *three* of the more important impurities which pig-iron may contain

Describe *one* method of converting pig-iron into steel. (N.U.J.M.B.)

2. State the essential chemical difference between the Bessemer and the open-hearth processes for the production of steel. What changes are common to both processes? What is the "basic Bessemer process," and why is it of importance? (Worcester Polytechnic Inst., U.S.A.)

3. Whence and by what processes is platinum obtained? What are its physical properties and how is it affected by being alloyed with iridium? Point out briefly the utility for chemical investigation of platinum, glass and indiarubber. (New Zealand Univ.)

4. Give an account of the compounds of nickel and cobalt, with special regard to the points of similarity and difference between the chemical properties of the two elements. (London B.Sc.)

5. Give an account of the ammine compounds of cobalt and platinum, clearly explaining how the constitution of typical compounds is usually represented. (Inst. of Chem.)

6. Describe and explain the types of isomerism exhibited by the ammine compounds of cobalt. (Oxford Univ.)

7. Describe the extraction of nickel from its ores and give an account of the properties of the element and its more important compounds.

8. How is platinum found in nature? Describe methods of obtaining it in a finely divided condition, and give one indication of the use of the metal in an inorganic chemical preparation. (Cape Univ.)

9. Describe briefly and explain the blast furnace process, giving the purpose of each ingredient of the charge. (Amherst Coll., U.S.A.)

10. How would you make (1) ferrous chloride from iron, (2) ferrous sulphide from ferrous chloride, (3) ferrous sulphate from ferrous sulphide, (4) ferrous hydroxide from ferrous sulphate? Write equations for the reactions after giving the descriptions of the processes and indicate the colour of the product in each case. (Sheffield Scientific School, U.S.A.)

11. Starting with iron filings, dilute sulphuric acid, and a solution of ammonia, describe how you would prepare a crystalline specimen of ammonium iron alum.

If you were given ammonium iron alum (as an unknown salt) to analyse qualitatively, write an account of your analysis in columns under the headings experiment, observation, inference. (Oxford Locals.)

12. What are the common ores of iron? Describe and explain how iron and steel are obtained from iron ore.

Why is there always carbon monoxide in the waste gases from a blast furnace? (Oxford Univ.)

13. Give a concise account of the preparation from iron of (a) ferrous ammonium sulphate and (b) ferric ammonium alum. Say briefly how you would estimate the percentage of iron in each compound. (O. & C.J.B.)

14. Describe the preparation of any *two* alums.

Illustrate the characteristics of a "transition" metal by reference to the compounds of *either* iron *or* chromium. (O. & C.J.B.)



## GENERAL

1. For each of the following laws (a) discuss the considerations which led to its enunciation, and (b) indicate limitations in its applicability: (i) Boyle's Law, (ii) Ostwald's Dilution Law, (iii) Raoult's Law, (iv) Dulong and Petit's Law. (N.U.J.M.B.)

2. Compare and contrast the properties of the commonest oxides of sodium, boron, carbon, and sulphur. (Oxford Univ.)

3. Describe (a) the manufacture of sodium hydroxide by the electrolysis of brine, and (b) the extraction of magnesium hydroxide from sea-water.

It is stated that when sodium hydroxide reacts with a non-metal simultaneous oxidation and reduction of the non-metal occur. Discuss by reference to the elements silicon, phosphorus, chlorine and sulphur how far and in what way this statement is justified. (N.U.J.M.B.)

4. Comment on, illustrate or explain *three* of the following statements:

(a) In the Periodic Table lithium is classed with the alkali metals, but some of its compounds resemble more closely those of magnesium and calcium.

(b) Hydrogen and sodium have one valency electron each. Sodium chloride is electrovalent but hydrogen chloride is covalent.

(c) The ion of a transition metal does not have eight electrons in the outer group.

(d) Sulphur can replace oxygen in (i) the oxidation of a sulphite; (ii) the reaction between arsenious oxide and a base. (O. & C.J.B.)

5. Comment on, illustrate, or explain *four* of the following statements:

(a) a catalyst does not alter the point of equilibrium in a reversible reaction.

(b) Combustion is not necessarily accompanied by flame.

(c) A colloidal particle carries an electric charge.

(d) Amorphous carbon absorbs gases easily, but diamond will not.

(e) The end point of an acid-alkali titration is not always at neutrality.

(O. & C.J.B.)

6. In the Periodic Classification, elements are arranged in (a) groups and (b) periods. Explain briefly how these arrangements can be related to the structure of the atoms concerned.

What general differences are there between the reactions of the alkali metals (Group IA) and their compounds, and those of the alkaline earth metals (Group IIA) and their compounds? (O. & C.J.B.)

7. If a volatile solute is added to a solvent what effects may be noticed in the total vapour pressure of the mixture? What difference would there be if the solute were non-volatile? Explain the importance of these observations *either* on the separation of two volatile liquids by distillation *or* on the determination of molecular weights in solution (O. & C.J.B.)

8. Give an account of the allotropy of *one* element showing monotropy and of *one* showing enantiotropy. Is it possible to apply either of these terms to the interconversion of oxygen and ozone? (O. & C.J.B.)

9. (a) Write ionic equations for the reactions which occur in aqueous solution between the following:

(i) ferric chloride and stannous chloride,

(ii) chlorine and ferrous sulphate in the presence of dilute sulphuric acid,

(iii) iodine and sodium thiosulphate.

Hence derive a definition of oxidation.

(b) In the light of your definition state, giving your reasons, which atom, molecule, or ion is oxidized in each of the following reactions:

(iv) zinc with dilute hydrochloric acid,

(v) hydrogen sulphide with sulphur dioxide,

(vi) manganese dioxide with concentrated hydrochloric acid. (N.U.J.M.B.)

10. Explain how you would demonstrate in the process of qualitative analysis the presence of (a) calcium and magnesium in the mineral dolomite (the double carbonate of these metals); (b) chlorine and copper in cuprous chloride; and (c) zinc and oxalate ion in zinc oxalate. (O. & C.J.B.)

11. Describe the chemical principles involved in the extraction of (a) lead from galena (PbS) and (b) zinc from blende (ZnS).

You are given a solution which is known to contain two metals only, in the form of their nitrates, and which you can show by analysis to be lead and zinc. Describe and explain the reactions you would carry out in order to obtain this answer. (O. & C.J.B.)

12. What is (a) the electrode potential of a metal, (b) the heat of formation of a metal oxide? What connection is there between the two?

Discuss by reference to these two quantities *two* of the following: (a) the thermite reaction between aluminium and metallic oxides; (b) displacement of metals from their salts; (c) reduction of metal oxides by hydrogen. (O. & C.J.B.)

13. State Faraday's Laws of Electrolysis. Describe, with the aid of diagrams, how you would use an electrolytic method (a) to determine the equivalent of a metal; (b) to purify a metal; and (c) to prepare pure oxygen. (O. & C.J.B.)

14. Give a definition of "melting point." Explain, from the viewpoint of the kinetic theory, what changes take place when the temperature of a solid is raised to the melting point.

Describe concisely how you would measure the melting point of a solid, of which only a few milligrams were available.

Explain carefully the differences between what takes place during the melting of pure and impure specimens of a substance, and show how the melting point may be used as a criterion of the purity and for the identification of substances. (N.U.J.M.B.)

15. Describe what may be seen, and state the chemical reactions which take place, when

- (a) ferrous sulphate crystals are heated;
- (b) a dilute aqueous solution of potassium cyanide is added, drop by drop, to a dilute aqueous solution of silver nitrate;
- (c) litmus is added to a solution of potassium cyanide;
- (d) water is added to "Plaster of Paris." (Cambridge Locals.)

16. By means of equations and brief notes on reaction conditions, indicate the methods by which the following may be prepared:

- (a) ferric sulphate from metallic iron,
  - (b) lead sulphate from metallic lead,
  - (c) anhydrous aluminium chloride.
- Write equations showing the effect of heat on (d) hydrated ferrous sulphate, (e) red lead, (f) silver nitrate. (N.U.J.M.B.)

17. Define the boiling point of a liquid. Explain how the boiling point of a mixture of two miscible liquids can vary with the relative amounts of each. Show how the compositions for the liquid and vapour in equilibrium with each other may be represented graphically.

Explain what is meant by "a constant boiling-point mixture," and how you would distinguish between a pure compound and a constant boiling-point mixture.

The vapour pressure of water at 40° C. is 54.9 mm Hg. Calculate the vapour pressure at 40° C. over a solution containing 1 gram. molecule of acetamide dissolved in 900 gram. of water. (N.U.J.M.B.)

18. Write an essay on *one* of the following subjects:

- (a) Allotropy, illustrating your answer by reference to the elements sulphur, phosphorus and tin.
- (b) The position of an element in the periodic system in relation to the preparation, properties and structure of its chlorides.
- (c) The electrochemical series of the elements and the phenomena that may be explained in terms of it. (N.U.J.M.B.)

19. Write an essay on *either* the liquefaction of gases *or* the inert gases. (N.U.J.M.B.)

20. Write a general account, with illustrative examples, of the application of physico-chemical principles in the purification of inorganic substances. In your account refer to gases, liquids and solids, and to elements and compounds. (N.U.J.M.B.)

21. Account for the following:

(a) A mixture of equal volumes of ethyl acetate and water, after standing for some hours, contains a much smaller proportion of acetic acid than a mixture of equal volumes of ethyl acetate and dilute hydrochloric acid.

(b) Addition of ferrous sulphate solution to silver nitrate solution produces a grey precipitate. After separation from the solution, this precipitate dissolves in dilute nitric acid to give a colourless solution which forms a white precipitate when dilute hydrochloric acid is added.

(c) A white precipitate is formed when ammonia solution is added to magnesium sulphate solution but no precipitate appears when ammonia solution is added to a mixture of magnesium sulphate solution and ammonium chloride solution. (Cambridge Locals.)

22. A specimen of each of the following substances is contained in a separate unlabelled bottle:

ammonium carbonate-

barium carbonate-

copper carbonate

sodium bisulphate

sodium carbonate

ammonium chloride — gives off  $\text{NH}_3$

calcium nitrate

copper nitrate — gives off  $\text{NO}_2$  (Also has  $\text{O}_2$ )

sodium borate (borax) — swells up forming beads

sodium chloride — deflagrates

Assuming that there are available test-tubes, ignition tubes, indicator papers and a lighted bunsen burner but no chemicals except water and the ten substances themselves, describe a procedure which will enable the bottles to be correctly labelled. (N.U.J.M.B.)

23. State and explain what you would observe in each of the following experiments:

(a) To a solution containing manganese and zinc ions, sodium hydroxide solution is added until finally the sodium hydroxide is in excess.

(b) Potassium iodide solution is added to a suspension of silver chloride in water.

(c) Stannous chloride solution is gradually added to mercuric chloride solution until the stannous chloride is present in excess.

(d) Metallic zinc is added to a solution of ferric sulphate acidified with dilute sulphuric acid. (N.U.J.M.B.)

24. Discuss the importance of the contributions made to chemical thought and practice by three of the following: Andrews, Cannizzaro, Faraday, Graham, Hess, Le Chatelier. (N.U.J.M.B.)

25. Describe briefly methods involving the use of electricity for the following industrial processes. (a) the extraction of aluminium from bauxite, (b) the purification of crude copper, (c) the manufacture of calcium carbide. State one important use for each of the products. (Cambridge Locals.)

26. Give a comparative account of the chemistry of sodium, magnesium and aluminium. (Cambridge Locals.)

27. Describe how (a) sodium cyanide, (b) potassium ferrocyanide, and (c) potassium dichromate may be prepared, and give an account of their properties and reactions. What would you expect to happen when, by using platinum electrodes, an aqueous solution of a ferrocyanide is electrolysed? (Cambridge Locals.)

28. Describe briefly (no diagram required) the methods used to produce three fuel gases of industrial importance. How may hydrogen be obtained from one of these fuels?

How, and under what conditions, does hydrogen react with (a) chlorine, (b) compounds of arsenic, (c) ethylene? (Cambridge Locals)

29. What is meant by the term *allotropy*? Using sulphur and phosphorus as illustrative examples, distinguish carefully between enantiotropy and monotropy.

How would you determine the transition temperature of rhombic and prismatic (monoclinic) sulphur? (Cambridge Locals.)

30. Write short notes on (a) deliquescence and efflorescence, (b) Van't Hoff's factor  $i$ , (c) diffusion of gases, and (d) Le Chatelier's principle. (Cambridge Locals.)

31. How would you detect:

(a) traces of ammonia in water;

(b) approximately 10 per cent nitrogen in oxygen;

(c) approximately 10 per cent of copper in silver;

(d) approximately 10 per cent of sodium sulphite in sodium sulphate;

(e) bromide and nitrate radicals in a mixture of sodium bromide and sodium nitrate? (Cambridge Locals.)

32. Give a *comparative* account of the properties of the hydrides of the common non-metallic elements. (Cambridge Locals.)

33. An element X forms an oxide  $X_2O_3$  which is amphoteric, and an oxide  $X_2O_5$  which is acidic. Suggest:

(a) a formula for an acid corresponding to each oxide;

(b) a method of preparing a pure specimen of the sulphide  $X_2S_3$ , which is insoluble in water;

(c) a method of preparing a pure specimen of the hydride  $XH_3$ ;

(d) the reaction occurring between X and concentrated nitric acid. (Cambridge Locals.)

34. Imagine that you were given a supply of a supposedly unknown element in the form of one of its oxides. Explain what you would do to attempt to find out the main features of its chemistry, and to allocate it to its correct place in the Periodic Table. (Inst. of Chem.)

35. How could you detect: (a) a chloride in the presence of bromide and iodide ions; (b) a carbonate in the presence of a sulphite; (c) a nitrate in the presence of a nitrite? In any *one* mixture indicate how the determination of the ion first mentioned could be carried out quantitatively. (Inst. of Chem.)

36. Describe in detail the preparation of *two* of the following, and state their more important chemical characteristics: sulphuryl chloride; chromyl chloride; potassium iodate. (O. & C.J.B.)

37. Write notes on the following: the allotropy of tin; principles used in the detection of acid radicals. (O. & C.J.B.)

38. Comment on or explain *three* of the following sentences with special reference to the words italicized:

(a) the *degree of dissociation* of a *weak electrolyte* at dilution  $V$  is the ratio of the *equivalent conductivity* at that dilution to the equivalent conductivity at *infinite dilution*.

(b) A weak acid in the presence of one of its salts constitutes a *buffer solution*.

(c) The *osmotic pressure* of a solution is the pressure necessary to prevent the *osmosis* of the solvent into that solution

(d) *Henry's Law* is the *partition law* (distribution law) applied to a liquid and a gas. (O. & C.J.B.)

39. *Either* compare the chemistry of bromine with that of iodine and fluorine, *or* compare the chemistry of silver with that of copper and gold. (Inst. of Chem.)

40. What can be deduced from the following observations:

(a) The osmotic pressure of 0.12 molar aqueous solution of  $Hg(CN)_2$  is 2.95 atmospheres at  $27^\circ C$ .

(b) The atomic weight of argon is greater than that of potassium. (Inst. of Chem.)

41. Describe in detail the preparation of pure, anhydrous specimens of (a) silver chloride, (b) ferric chloride, (c) calcium chloride.

Explain why the methods of preparation are so different in the three cases. (Cambridge Locals.)

42. From knowledge of their physical and chemical properties, what can you

infer concerning the nature of the valency forces in the substances of empirical composition  $\text{KBr}$ ,  $\text{HCl}$ ,  $\text{PbO}_2$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ , and  $\text{HgCl}_2$ ? (Cambridge Locals.)

43. Define the term "equivalent conductance." Show why the concept of equivalent conductance at infinite dilution is of particular importance in discussing both weak and strong electrolytes. Describe, without experimental details, how you would determine the equivalent conductance at infinite dilution of acetic acid in water. (Inst. of Chem.)

44. Select *one* of the elements cadmium, aluminium, or arsenic, and give an account of its chemistry, pointing out carefully in what ways it may differ in behaviour from the elements immediately above and below in the Periodic Table. (Inst. of Chem.)

45. Write a comparative account of the chemistry of *one* of the following groups of elements: (a) iron, cobalt and nickel; (b) zinc, cadmium and mercury; (c) molybdenum, tungsten, uranium. (Inst. of Chem.)

46. "When an element exists in several valency states, the lowest oxide is generally basic, the highest acidic, and oxides of intermediate valency more or less amphoteric." Discuss this statement with reference to elements in various parts of the Periodic Table, and suggest an explanation for it. (Inst. of Chem.)

47. Classify the hydrides of the elements and describe characteristic properties of each class. (Inst. of Chem.)

48. Describe the preparation of *four* of the following substances. State their uses and comment on any points of chemical or structural interest: (a) zinc dithionite (hydrosulphite); (b) chlorine dioxide; (c) uranium hexafluoride; (d) hydrazine; (e) iron pentacarbonyl; (f) sodium hexametaphosphate. (Inst. of Chem.)

49. Discuss features of interest in the preparation, structure and chemical properties of *three* of the following: (a)  $\text{P}_4\text{O}_{10}$ ; (b)  $\text{ClO}_2$ ; (c)  $\text{SO}_3$ ; (d)  $\text{N}_2\text{O}_4$ ; (e)  $\text{H}_2\text{O}_2$ .

50. How could anhydrous samples of the chlorides of boron, carbon, nitrogen, and oxygen be prepared? What are their physical properties? Describe how each reacts with water and comment on, and explain, any striking differences in behaviour. In what respects, and why, does the action of water on these chlorides differ from the action of water on the corresponding fluorides? (Inst. of Chem.)

51. What factors determine the distribution of a solute between two immiscible solvents? Give examples of the practical applications of such partitions

A substance X is twice as soluble in benzene as it is in water, the molecular weight being the same in both solvents. Compare the weights of X extracted from 100 c.c. of aqueous solution (a) by the use of 100 c.c. of benzene in one operation, (b) by two successive applications of 50 c.c. of benzene each. (O. & C. J. B.)

52. How would you prepare *two* of the following: (a) a concentrated solution of hydriodic acid; (b) anhydrous aluminium chloride; (c) carbonyl chloride (phosgene); (d) phosphorus pentachloride?

Describe the properties and reactions and give one use of each of the substances you select. (Oxford Univ.)

53. Show how the chemical properties of *either* (a) sulphur, selenium and tellurium, *or* (b) chlorine, bromine and iodine, vary with increase in atomic number. (Inst. of Chem.)

54. Describe how you would prepare the following: (a) zinc oxide from brass; (b) sodium thiosulphate from sodium hydroxide, sulphur dioxide, and sulphur; (c) anhydrous magnesium chloride from magnesium oxide, (d) calcium nitrate from calcium sulphate. (Oxford Locals.)

55. How can the phenomenon of osmosis be explained? Describe *one* method for the measurement of osmotic pressure. What are the basic assumptions which are made in deriving the ideal gas laws from the kinetic theory of gases? (Oxford Univ.)

56. Describe the additions and alterations made to the Periodic Table and the development of our understanding of it since it was first put forward by Mendeléeff. (Oxford Univ.)

57. Give an account of the manufacture (without technical details) of sulphuric and nitric acids. *Either* explain the industrial importance of these substances *or* explain their principal uses in the laboratory.

58. Write an essay on *either* "The non-metallic elements," or "The extraction of metals from their ores."

59. Discuss factors which are responsible for the shapes of simple covalent inorganic molecules containing not more than two elements. (Inst. of Chem.)

60. Of recent years a number of the "less common" elements have assumed considerable economic importance. Select one of these, describe how it is obtained from naturally occurring sources, outline its chemistry, and explain wherein its importance lies. (Inst. of Chem.)

61. Give a general account of the structure of the Periodic Table, with special reference to the principles underlying the distribution of electrons among different energy levels and the order in which these levels are occupied. (Inst. of Chem.)

62. Make a comparison between the simpler hydrides of the elements boron, carbon, nitrogen, oxygen and fluorine. To what extent are the formulae and properties of these hydrides those to be expected from the position of these elements in the Periodic Table? (Inst. of Chem.)

63. Describe clearly, but without practical details, one method each for the experimental determination of  $R$  (the gas constant),  $F$  (the faraday) and  $N$  (the Avogadro number). (Inst. of Chem.)

64. Explain clearly what is the action of heat on the following: aluminium chloride; phosphorus pentachloride; potassium chlorate; mercuric nitrate; hydrogen fluoride. (Oxford Univ.)

65. Describe the preparation of *four* of the following: chromyl chloride; barium peroxide; nickel carbonyl; sodium persulphate; arsenic trioxide. (State briefly the interesting features of any *one* of the compounds you have chosen.) (Oxford Univ.)

66. Describe briefly the manufacture and discuss the industrial and economic importance of *two* of the following: oxygen; sodium carbonate, nitric acid; ethylene; water gas. (O. & C.J.B.)

67. Explain concisely the difference between *three* of the following: (a) a weak and a strong electrolyte; (b) electrovalency and covalency; (c) cooling by adiabatic expansion and the Joule-Thomson effect; (d) dissociation and thermal decomposition; (e) monotropy and enantiotropy. (O. & C.J.B.)

68. Explain what you understand by the terms (a) solubility product, (b) specific conductivity; (c) partition coefficient. Give an account of how you would proceed to determine *one* of these for some named substance. (Oxford Univ.)

69. Transition metals are said to be characterized by coloured ions, variable valency, catalytic activity, and the formation of complex ions and compounds. Illustrate these characteristics by examples from the chemistry of iron and *either* manganese or nickel. (O. & C.J.B.)

70. Explain the formation of a white precipitate:

(a) when hydrogen chloride is passed into a cold saturated solution of sodium chloride;

(b) when a concentrated solution of bismuth chloride is added to a relatively large volume of distilled water;

(c) when ammonium hydroxide solution is added to a solution of magnesium sulphate;

(d) when potassium cyanide solution is added to silver nitrate solution.

Why does the precipitate in (d) dissolve in excess of potassium cyanide solution? (Oxford Locals.)

71. The element calcium has an *equivalent* of 20.04, its *atomic weight* is 40.08, its *atomic number* is 20, and there are several calcium *isotopes*. What do you understand by the terms printed in *italics*? Point out any ways in which these terms are connected.

Give the electronic structures of calcium oxide and calcium chloride. (Oxford Locals.)

72. Select *two* of the metals iron, aluminium and copper. Describe briefly their extraction from their ores, how their properties may be modified by alloying, and how their salts may be identified. (O. & C.J.B.)

73. Show, with examples, what chemical reactions are typical of (a) metal; (b) an amphoteric oxide, (c) an acidic oxide; (d) a reducing agent. (Oxford Univ.)

74. What experiments would you make to find out whether:  
 (a) a given specimen of water is temporarily hard, permanently hard, or soft;  
 (b) a gas-jar contains nitrous oxide or a mixture of nitrogen and oxygen;  
 (c) a substance is sodium sulphide or sodium sulphate? (Oxford Univ.)
75. Give an account of the experimental evidence from which it is deduced that the molecular formula of water is  $H_2O$  and the formula of carbon monoxide is  $CO$ . (Oxford Univ.)
76. Describe the chemistry of *either* manganese *or* lead. (Oxford Univ.)
77. Compare the chemistry of oxygen with that of sulphur. (Oxford Univ.)
78. Describe in detail the laboratory preparation of *four* of the following:  
 (a) cuprous iodide; (b) an aqueous solution of perchloric acid; (c) mercurous chloride;  
 (d) iodine pentoxide; (e) anhydrous hydrogen bromide. (Oxford Univ.)
79. Give a general account of the chemistry of *either* silicon *or* magnesium. (Oxford Univ.)
80. Give an account of *either* cuprous and cupric compounds *or* mercurous and mercuric compounds. (Oxford Scholarships.)
81. Write notes on *three* of the following: alums; basic salts; amphoteric oxides and hydroxides; metal hydrides; peroxides. (Oxford Scholarships.)
82. Give an account of the physical and chemical properties of metallic compounds which are comparatively volatile. (Oxford Scholarships.)
83. Compare and contrast the properties of compounds having the formula  $XO_3$ , in which X is a metal or non-metal. (Oxford Scholarships.)
84. Comment on features of interest in the chemistry of *three* of the following compounds: ozone, hydrogen fluoride, hydrogen peroxide, hydrazine, potassium chromate. (Oxford Scholarships.)
85. The compounds  $NCl_3$ ,  $AlCl_3$ ,  $PCl_3$ ,  $AuCl_3$ ,  $BiCl_3$ , and  $FeCl_3$  have the same formula type. Do you expect them to have similar properties? (Oxford Scholarships.)
86. Comment on the interesting features of the hydrides of elements. (Oxford Scholarships.)
87. Write an essay on *either* "Variable Valency" *or* "Oxidation and Reduction." (Oxford Scholarships.)
88. What are the principles which are used in determining (a) molecular weights, (b) atomic weights?  
 How would you determine the molecular weight of ammonia and the atomic weight of nitrogen? (Oxford Scholarships.)
89. Write notes on *two* of the following: (1) the discovery of the rare gases; (2) isomorphism; (3) salt hydrates. (Oxford Scholarships.)
90. Discuss methods which might be used for obtaining pure samples of each of the following: iron, silicon, bromine. (Oxford Scholarships.)
91. Describe briefly the preparation of the hydrides of phosphorus, sulphur and chlorine. Discuss their chemical properties in relation to the positions occupied by the three elements in the periodic table. (Oxford Scholarships.)
92. Describe, with sufficient experimental detail, how you would prepare *four* of the following: potassium perchlorate; sodium thiosulphate, lead dioxide; phosphine; sulphuryl chloride; stannic chloride; iodine pentoxide. (Oxford Univ.)
93. Write equations for the reactions between:  
 (a) oxalic acid, potassium permanganate and dilute sulphuric acid;  
 (b) sodium thiosulphate and iodine;  
 (c) potassium chromate and silver nitrate;  
 (d) barium chloride and sodium carbonate.
- Write brief notes on the uses of reactions (a), (b), and (c) in volumetric analysis.
- How would you collect and estimate the purity of the barium compound formed in (d)? (Cambridge Locals.)
94. Compare the chemistry of beryllium and aluminium. (Inst. of Chem.)
95. Starting from commonly available materials, indicate how you would prepare reasonably pure samples of *four* of the following oxides:  $ClO_2$ ;  $SeO_2$ ;  $GeO_2$ ;  $CeO_2$ ;  $BaO_2$ ;  $KO_2$ . Mention any points of special interest in connection with the

oxides you select and write equations for their reactions (if any) with aqueous potassium hydroxide and with concentrated hydrochloric acid. (Inst. of Chem.)

96. Give a comparative account of the hydrides of the elements, paying particular attention to the methods available for their preparation and their chemical and physical properties. (Inst. of Chem.)

97. Write an essay on *one* of the following topics:

(a) The hydrogen bond.

(b) The actinide elements. (Inst. of Chem.)

98. Explain with illustrative examples *four* of the following terms: co-ordination compound, polymer, polymorphism, colloid, weak acid. (Oxford Scholarships.)

99. Explain briefly *three* of the following terms: supersaturated solution; decinormal solution; colloidal solution; polymer; isotope. (Oxford Scholarships.)

100. Some elements exhibit more than one valency in their compounds with oxygen. By reference to *three* elements discuss how the properties of the oxides of an element vary as the valency changes. (Oxford Scholarships)

101. In the following examples identify *two* of the three substances X, Y, Z, and explain briefly the reactions involved:

(a) A black solid X dissolved in water to give a blue solution, which, on the addition of hydrogen sulphide, gave a black precipitate insoluble in dilute hydrochloric acid but soluble in moderately concentrated nitric acid. When added to the solution of the precipitate in nitric acid, ammonium hydroxide produced a blue precipitate soluble in excess of ammonium hydroxide. On heating X with concentrated sulphuric acid, an acid vapour was given off which had a reddish colour, and part of which condensed to a reddish-brown liquid.

(b) Y was a white solid which gave a colourless solution in water. When added to this solution, silver nitrate solution gave no precipitate, but barium nitrate produced a white precipitate which was insoluble in dilute acids. On heating Y with dilute hydrochloric acid there was no reaction, but when it was heated with concentrated sulphuric acid, a fuming vapour was given off which dissolved in water to give an acid solution. On electrolysis of either a dilute or concentrated aqueous solution of Y hydrogen was given off at the cathode and oxygen at the anode. A solution of Y gave a yellow precipitate with sodium cobaltinitrite solution, but did not colour a bunsen flame.

(c) Z was a purple salt which dissolved in water to give a solution that turned green on heating. Sodium hydroxide precipitated from this solution a green hydroxide soluble in excess of the alkali. On adding hydrogen peroxide to the alkaline solution the solution became yellow. On adding more hydrogen peroxide and acidifying a blue solution was produced, which turned green on standing, with evolution of oxygen. The solution of Z in water gave a white precipitate with barium chloride solution, which was insoluble in dilute acids. A solution of Z in concentrated hydrochloric acid coloured a bunsen flame lilac. (O. & C.J.B)



## ANSWERS TO QUESTIONS

## CHAPTER 2

2. 11 protons, 12 neutrons.

## CHAPTER 3

1. Vap. Dens, 63.1. Vapour is associated.
2. Vap. Dens, 14
3. Partial pressures ammonia, 22.22 atm, nitrogen, 44.44 atm., hydrogen, 133.33 atm.
7. 39.93.
14.  $4.6 \times 10^4$  cm. per sec

## CHAPTER 5

1. 200.  
7 56.23%
4. (a) 54.67, (b) 109.34.

## CHAPTER 6

2. 11·0 gm per litre                      3. (a) 9, (b) 12·14

## CHAPTER 7

3. 8·67, 52, 3,  $\text{XO}_3$ .      9    183·66.      13    200·6, 199·4

## CHAPTER 8

1.  $\text{MO}_3$  4 32.75.  
5 (a) 6.22 litres, (b) 12.44 litres, (c) 12.44 litres  
9 0.95 l  
10 29.72 grm, 4.73 litres,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $6\text{H}_2\text{O}$ .

## CHAPTER 13

- |     |  |    |            |
|-----|--|----|------------|
| 2   | 20.69 grm per 100 grm                        | 3  | 148.5      |
| 4   | 3.925 grm                                    | 5  | 1.527      |
| 7   | 66.67% nitrogen, 33.33% oxygen               | 11 | 5.441 kgm. |
| 13  | 19.73 c.c., 14.77 c.c., 7.72 c.c., 0.28 c.c. |    |            |
| 14. | (a) 24.5°, 36°, (b) 31 grm                   |    |            |

## CHAPTER 14

1. 345·7.                      2 (a) 124·34, (b) 55·12%.
6. 211·4                      11. 699·7.

## CHAPTER 15

2. 32-71. 14. 82-19%  
16. 0-0072 grm oxygen, 0-0283 grm. copper, 0-032 grm chlorine.  
17. 3-195 grm chlorine, 0-72 grm. oxygen, 2-831 grm. copper, 9-700 grm.  
silver.  
18. 0-0376 mhos, 376-4 mhos.

## CHAPTER 16

2. 64.3 units.                      3. (iv) 25,600 cal.                      4. 19,700 cal.  
 5. 48,000 cal.                      6. 87 Cals.                      7. 113 Cals  
 8. 1318 K.                      9. (a) 54.5 Cals, (b) 44.6 Cals.

## CHAPTER 17

2. 2.87                      14.  $5 \times 10^{-3}$  gm-ion per litre  
 15. 0.041.

## CHAPTER 18

7.  $1.58 \times 10^{-5}$  gm. per litre.                      8. 5.12  
 10.  $1.79 \times 10^{-5}$ .                      12. 475.                      13. 2.87  
 14.  $9.54 \times 10^{-6}$ ; 0.129 N.                      16.  $1.1 \times 10^{-10}$ .  
 20.  $1.215 \times 10^{-8}$ ,  $1.102 \times 10^{-4}$  gm. per litre  
 21.  $\text{H}_2 = \text{CO}_2 = 32.1\%$ ,  $\text{H}_2\text{O} = \text{CO} = 17.9\%$  (a) the same, (b) less.

## CHAPTER 20

9. 44.8 litres.                      10. 0.204%  
 12. (a) 89.6 litres, (b) 44.8 litres, (c) 89.6 litres.  
 15. 33.88 gm.

## CHAPTER 21

2. 3.03 gm. per litre.

## CHAPTER 22

5.  $\text{C}_2\text{H}_2$ .

## CHAPTER 26

2.  $7.4 \times 10^{23}$ .

## CHAPTER 37

3. +3.

## GENERAL

17. 53.8 mm                      51.  $a : b = 8 : 9$ .

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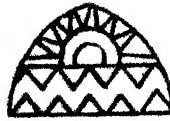
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